

# ABSTRACT OF THESIS

Name of Candidate ..... **JOHN ANGUS McDIARMID BAYNE** .....

Address ..... **[REDACTED] St [REDACTED] [REDACTED]** .....

Degree ..... **Doctor of Philosophy** ..... Date ..... **July 1976** .....

Title of Thesis ..... **Aspects of Palladium-Assisted Reactions of Alkenes** .....

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This thesis describes a study of the palladium-assisted arylation of alkenes. A review of the work of contributors in this and related fields is given.

In the course of the present work it was found that consistent yields of phenylation products could not be obtained in the reaction between benzene and styrene assisted by palladium acetate. Palladium acetate of sufficient purity to produce consistent results over the initial period of reaction was obtained from a study of the methods of preparation and purification of the acetate.

Mechanistic investigations were performed and a series of reactions is described in which benzene and a substituted benzene compete for a limited amount of styrene. The results suggest that alkene arylation is similar to electrophilic aromatic substitution. A similar series of reactions in which excess benzene reacted with equimolar amounts of styrene and a ring-substituted styrene showed no large variation in the reactivity of the styrene.

Reactions were performed in which the molar ratio of the reactants of styrene phenylation were varied, analysis being carried out for the monophenylation, diphenylation and alkene coupled products. The results indicate that reaction through a complex formed between the alkene and palladium is probable and not, as previously postulated through a  $\sigma$ -arylpalladium species. This conclusion was supported by comparison of the rate of stilbene formation in the 'normal' phenylation with its rate of formation in a reaction in which styrene was added to the attempted phenyl coupling reaction mixture.

Several short studies related to styrene phenylation were performed: the phenylation of alkenes other than styrenes; temperature dependence of styrene phenylation; styrene phenylation assisted by palladium compounds other than palladium acetate and the use of u. v. and n. m. r. spectroscopy to study styrene phenylation. None of these studies proved to be of great value in the elucidation of the mechanism of alkene arylation.

Attempts were also made to effect cyclisation of various alkenes, none of which was largely successful.

*Use other side if necessary.*

ASPECTS OF PALLADIUM-ASSISTED  
REACTIONS OF ALKENES

by

John Angus McDiarmid Bayne, B.Sc.

Thesis presented for the degree of Doctor of Philosophy



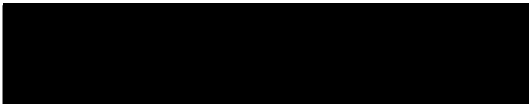
University of Edinburgh

1976

## DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes the results of research carried out in the Department of Chemistry, University of Edinburgh under the supervision of Professor J. I. G. Cadogan, and Dr. I. H. Sadler between October 1972 and September 1975.



### Acknowledgements

I would like to express my appreciation and thanks to my supervisors, Professor J. I. G. Cadogan and Dr. I. H. Sadler for their guidance and encouragement throughout the course of this work.

Thanks are due to various other members of Edinburgh University Chemistry Department: to Dr. P. C. Bell for mass spectra; to Mr. John Grunbaum for elemental analyses and to Mr. Tom Naisby for technical assistance. I am grateful to Mrs. C. G. Ranken for her skill and patience in typing the thesis and to Mr. Colin Baxter for the photographs.

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I am grateful to Drs. Fletcher and Wigglesworth of the British Petroleum Company's Epsom Research Centre for their interest and for a sample of palladium acetate. I thank the British Petroleum Company Ltd., for the generous award of a Studentship during the tenure of which this work was carried out.

### Postgraduate Lectures

I attended the following lectures to obtain the required number of eight units for postgraduate study.

- |     |  |         |
|-----|--|---------|
| (1) | Three years' attendance at Laboratory 10 research group seminars   | 3 units |
| (2) | A series of five lectures by Professor P. L. Pauson: Organometallic Processes in Organic Chemistry             | 1 unit  |
| (3) | A series of five lectures by Dr. A. J. Bellamy: Recent Developments in the Theory of Concerted Processes       | 1 unit  |
| (4) | A series of five lectures by Dr. G. Tennant: Molecular Rearrangements  | 1 unit  |
| (5) | A series of five lectures by Dr. B. Capon: Carbonium Ions  | 1 unit  |
| (6) | A series of five lectures by various members of Shell Research Ltd.: Chemical Aspects of Oil Products Research | 1 unit  |

## ABSTRACT

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In the course of the present work it was found that consistent yields of phenylation products could not be obtained in the reaction between benzene and styrene assisted by palladium acetate. Palladium acetate of sufficient purity to produce consistent results over the initial period of reaction was obtained from a study of the methods of preparation and purification of the acetate.

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## INTRODUCTION

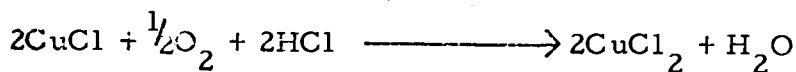
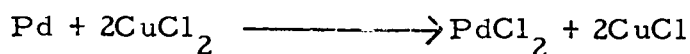
## INTRODUCTION: CONTENTS

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## 1. HISTORICAL DEVELOPMENT

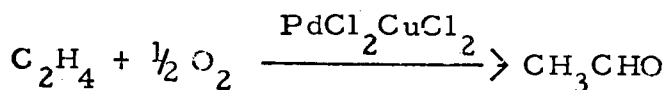
When ethylene is passed into aqueous palladium chloride, the initially brown solution turns black due to the precipitation of finely dispersed palladium metal, precipitation being accompanied by formation of acetaldehyde. This reaction was reported in 1894 by F.C. Phillips<sup>1</sup> who carried out investigations into methods of analysis of natural gas from Western Pennsylvania.

Apart from its use as a procedure for the separation and analytical determination of palladium,<sup>2</sup> the reaction between ethylene and palladous chloride to form acetaldehyde and palladium metal was neglected for about sixty years. In 1956, however, a group of workers led by J. Smidt, of the Consortium für elektro-chemische Industrie G.m.b.H. developed a process, based on Phillips' reaction, for the continuous production of acetaldehyde from ethylene.<sup>3, 4, 5</sup> The key to this process, known as the Wacker process (Wacker-Chemie being the parent company), was the discovery that, in the presence of copper (II) chloride and air, palladium (0) could be re-oxidised to palladium (II) and thus the reaction became catalytic in palladium. The Wacker process may be expressed by the following reaction sequence, (Scheme 1):



Scheme 1

This gives as the overall reaction:



The neglect of the ethylene oxidation reaction was probably because it did not seem an attractive proposition to produce the low-priced chemical, acetaldehyde, by the stoichiometric consumption of

a noble metal salt. The realisation that adjustment of the reaction conditions enabled palladium to be used catalytically, instead of stoichiometrically, provided the stimulus for the sudden development of interest in the interaction of transition metals, especially palladium, with unsaturated compounds.<sup>6</sup>

Mechanistic studies indicated that the ethylene oxidation step in the Wacker process occurred via nucleophilic attack on an ethylene-palladium chloride complex.<sup>4</sup> Consequently, van Helden investigated the possibility of nucleophilic attack by acetate on palladium-complexed aromatic compounds<sup>7</sup> and found that aromatic compounds react to yield biphenyls. In the absence of acetate, however, no biaryls were formed. This reaction was also noted by Davidson and Triggs<sup>8, 9</sup> who proposed the involvement of a  $\sigma$ -bonded palladium-aryl complex, since other metals yield stable aryl derivatives under identical conditions.

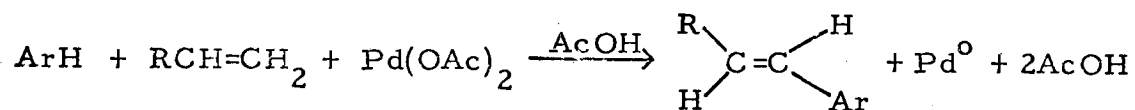
Another reaction involving the oxidative coupling of two organic species was described by Moritani and co-workers.<sup>10-14</sup> A high yield of stilbene was obtained by heating under reflux for eight hours, a solution of benzene, styrene and palladium (II) acetate in glacial acetic acid.<sup>11</sup> In later papers they demonstrated the wider applicability of the reaction<sup>15-23</sup> and how a measure of palladium re-oxidation was possible.<sup>13, 15</sup> Mechanistic studies<sup>24-29</sup> were also carried out.

A year after Moritani's original communication, Heck published a series of papers<sup>30-36</sup> describing a similar reaction in which the aryl group was present in the form of an arylmercury salt. Heck has since reported another oxidative coupling reaction of alkenes with aromatic compounds<sup>37, 38</sup> and has investigated the mechanisms of both reactions.<sup>37-40</sup>

Other workers<sup>41-48</sup> have reported significant advances in this field.

## 2. PALLADIUM-ASSISTED ARYLATION OF ALKENES

The replacement of one of the vinylic hydrogen atoms in an alkene by an aryl group, in the presence of a palladium compound, was described by Moritani.<sup>15</sup> The general reaction may be represented:

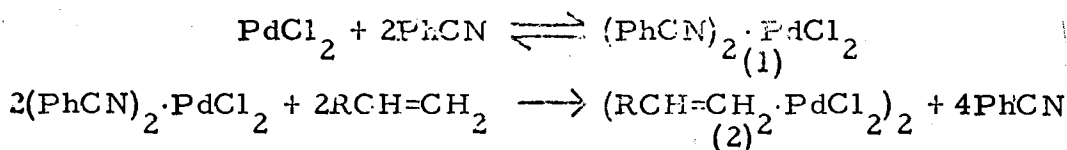


The two reacting organic species are oxidatively coupled, with concomitant reduction of Pd(II) to Pd(0). As described, palladium-assisted arylation of alkenes is of no synthetic or industrial use because a stoichiometric amount of palladium acetate is required. Work has been carried out with a view to making the reaction catalytic in palladium.<sup>13, 15, 41, 48</sup>

Volger had shown that, with the reaction mixture less the aromatic compound but in the presence of sodium acetate, oxidative coupling of the alkene occurred.<sup>49</sup> Van Helden had already described biaryl formation by the coupling of two aromatic species in the presence of palladium (II) chloride, sodium acetate and acetic acid,<sup>7</sup> and Davidson and Triggs had reported a similar coupling in the presence of palladium acetate.<sup>8, 9</sup> It is perhaps surprising, therefore, that alkene arylation occurs without biaryl formation and with only a few per cent coupled alkene. Moritani also observed acetoxylated alkenes in small yields.

Moritani has used the salt mixture for the arylation of alkenes but the yields of product alkenes were not as high as with palladium acetate.<sup>11</sup> Alkenes present as the alkene-palladium chloride complex have also been arylated.<sup>10, 11, 12</sup>

Alkene-palladium chloride complexes (2) were first prepared by Kharasch<sup>50</sup> who, after several unsuccessful attempts at formation of the complex by reaction of the alkene and palladium chloride in various solvents, succeeded by first preparing the benzonitrile-palladium chloride complex (1), (Scheme 2).



Scheme 2

Reaction of the alkene with the benzonitrile-palladium chloride complex (1) afforded the alkene-palladium chloride complex (2). The alkene complexes decompose, in the solid state at room temperature, on heating and in solution, liberating the alkene.

In Moritani's arylation reaction, the alkene and palladium compound were present in equimolar amounts, the aromatic species in one hundred-and-twenty fold excess, and acetic acid, which is essential for the reaction, in forty-three fold excess, relative to the alkene. The hydrogen atom replaced is lost from the least substituted olefinic carbon<sup>12, 15</sup> but yields of arylated alkenes decrease as the crowding of the double bond increases. (Table 1).

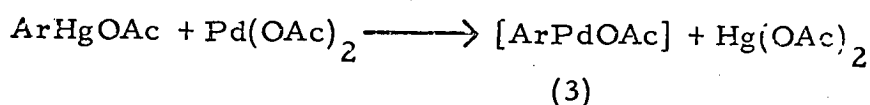
Table 1.      Reaction of Phenyl-Substituted Ethylenes with  
Benzene in the Presence of Palladium Acetate<sup>14, 15</sup>

Alkene	Product	Yield %
styrene	<u>trans</u> -stilbene	90
1, 1-diphenylethylene	triphenylethylene	72
<u>trans</u> -stilbene	triphenylethylene	28
triphenylethylene	tetraphenylethylene	13

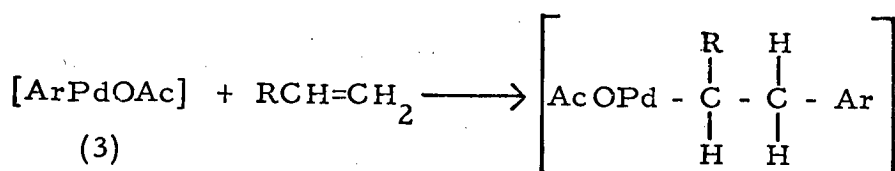
### 3.      RELATED ARYLATION REACTIONS

Arylation reactions, other than Moritani's,<sup>15</sup> assisted by palladium or by palladium compounds have been reported. The products formed are similar to those observed by Moritani, but the form in which the arylating group is added differs from Moritani's reaction.

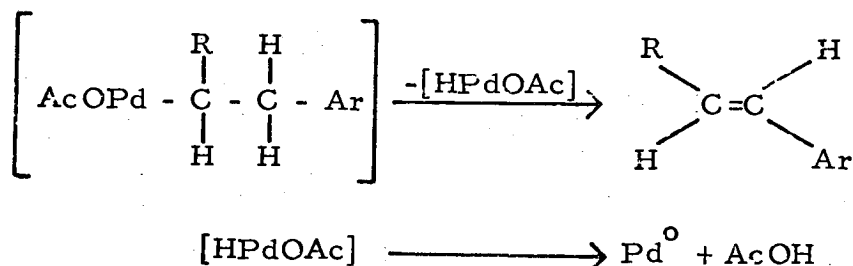
The most investigated is that cited by R. F. Heck<sup>30, 39, 40</sup> in which the aryl group is present as an arylpalladium complex formed in situ from the corresponding arylmercuric acetate and a palladium salt, either lithium palladium chloride or palladium acetate. The arylmercuric salt, palladium compound and alkene are mixed and heated in a suitable solvent such as methanol, acetonitrile or acetic acid. Reaction times range from a few minutes to several hours and the yields of product alkene vary widely. The first and important step is formation of an aryl-carbon to palladium  $\sigma$ -bond to give the intermediate, arylpalladium acetate (3).<sup>30</sup>



The composition of arylpalladium acetate (3) is not yet known. It is solvated or complexed with other materials in the reaction mixture but these other coordinating groups are not known. The second step is alkene insertion into the aryl-carbon-palladium bond of arylpalladium acetate (3).



The inserted product then loses the elements of palladium and acetic acid to yield the product alkene.



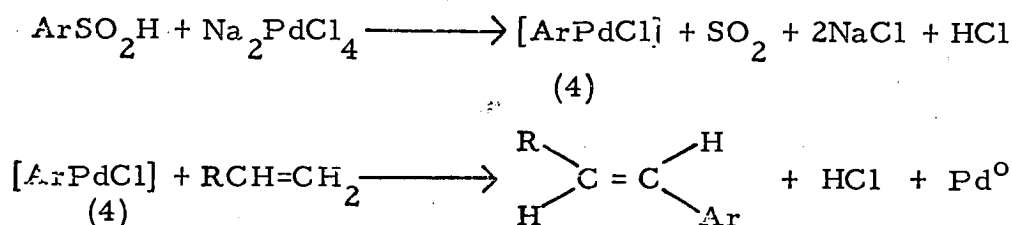
The  $\text{Pd}(0)$  formed can be re-oxidised to  $\text{Pd(II)}$  by  $\text{Cu(II)}$  salts.<sup>30</sup>

Heck has investigated in some detail the steric, electronic and solvent effects of the above process and has found that steric factors are the most important, and so the predominant product is that formed with least steric interaction.<sup>39, 40</sup> He has suggested

that palladium is effectively the smallest part of the organopalladium acetate (3),<sup>40</sup> so addition of the organic group is to the least substituted olefinic carbon. However, no study of the nature of the arylpalladium intermediate (3), has been reported.

Apart from hydrocarbon alkenes,<sup>30</sup> other unsaturated systems have been arylated, including allylic alcohols,<sup>31</sup> allylic halides,<sup>32</sup> enol esters,<sup>33</sup> vinyl ethers,<sup>33</sup> vinyl halides<sup>33</sup> and carbon monoxide.<sup>36</sup> Alkenes also undergo palladium-assisted methylation,<sup>30, 51</sup> and carboxyalkylation<sup>30</sup> with methylpalladium derivatives and carboxy-alkylpalladium derivatives respectively.

Selke<sup>45</sup> and Garves<sup>52</sup> published the results of studies into the expulsion of sulphur dioxide from aryl sulphinates and arene-sulphinic acids respectively, in the presence of palladium salts. Garves' reaction is thought to proceed, in a suitable solvent, such as ethanol or methanol, as shown in Scheme 3.



Scheme 3

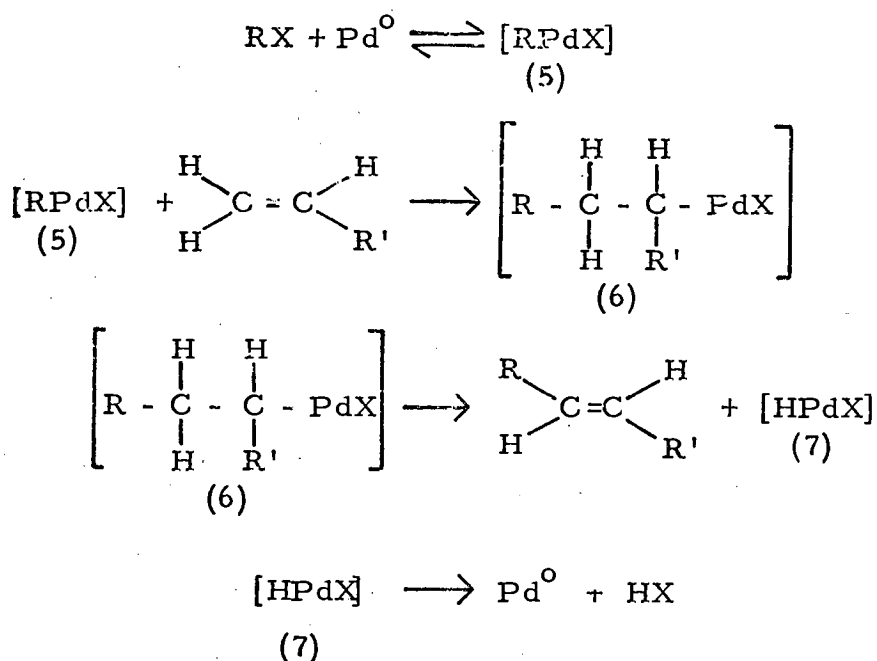
It is probable that the arylpalladium species (4), reacts with the alkene in a similar fashion to the reactive species (3) in Heck's reaction.<sup>30</sup> The reaction with aryl sulphinates<sup>45</sup> is thought to proceed in a similar manner. Yields of arylated alkene are improved by addition of mercuric chloride, and again palladium is recycled using cupric chloride.

Heck<sup>37</sup> and Mizoroki *et al.*<sup>53, 54</sup> have independently reported a palladium-catalysed arylation of olefinic compounds by aryl halides, normally the iodide. The alkene, aryl iodide and a catalytic amount of palladium acetate<sup>37</sup> or palladium chloride<sup>54</sup> are heated at 100° for two to seventy-two hours to give the product alkene in variable yields. In this reaction, palladium metal, prepared by *in situ* reduction of the palladium (II) compound by olefin, reacts with the organic halide



forming a very reactive solvated organopalladium (II) halide (5).

Heck suggests that the reactive organopalladium halides (5) are identical to those produced in the exchange reaction between palladium halides and organomercury compounds.<sup>30</sup> When prepared in the presence of an alkene the organopalladium halide (5) undergoes an addition reaction with the alkene, the adduct (6) formed decomposing by elimination of the elements of palladium and hydrogen halide to give the arylated alkene.<sup>37</sup> (Scheme 4).



Scheme 4

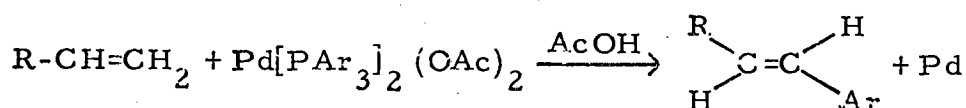
The palladium formed by decomposition of the hydridopalladium halide (7) is now available to go through another reaction cycle. It is the formation of palladium in the final step which is important because now no additional oxidant is required and so the reaction is catalytic in Pd (0). Hydrogen halide is also formed in the final step and since acid inhibits the arylation, a base is necessary to neutralise this acid. Potassium acetate<sup>53, 54</sup> and tri-n-butylamine<sup>37</sup> have been used for this purpose. Benzyl and styryl halides undergo a similar reaction but, in all cases, one of the more labile halogens, bromine or iodine, is necessary.<sup>37</sup>

A similar system in which palladium deposited on charcoal is the catalyst has been investigated by Julia et al.<sup>55, 56</sup> However,

they found that this arylation worked well only for styrenes.

Recently, Heck reported a variation on his palladium (0)-catalysed arylation of alkenes,<sup>38</sup> in which the catalyst is composed of palladium acetate and two equivalents of triphenylphosphine. The advantage of this catalyst is that loss of stereochemistry is reduced markedly.

Kikukawa<sup>46, 47</sup> also described an alkene arylation by palladium acetate and triarylphosphine, no other aryl compound being necessary. Product alkenes are formed when a mixture of palladium acetate, triarylphosphine and alkene, in acetic acid, are heated at 50°.



An aryl group from the phosphine is transferred to the alkene. The fate of the dearylated phosphine is, however, undetermined. Little mechanistic work has been carried out but Kikukawa<sup>47</sup> proposes the intermediacy of an arylpalladium species.

Phenylation of alkenes by organosilicon compounds in the presence of palladium salts has been studied by Akhrem *et al.*<sup>57, 58</sup> They observed that palladium (II) chloride cleaved silicon-carbon bonds in organosilicon compounds such as tetraalkyl-, trialkyl- and aryltrialkylsilanes; the alkyl or aryl group removed from the silane, being transferred to the alkene. Styrene, the silane and lithium palladium chloride (1:2:1) in tetrahydrofuran at 60° react to form stilbene in 94 per cent yield.

The mechanism proposed for this cleavage of organosilanes involves formation of alkyl or arylpalladium chloride, which is similar in form to the reactive palladium species (5).



The alkyl or arylpalladium chloride then reacts with alkene in a similar manner to the organopalladium halide [(5), Scheme 4]. The mechanism is analogous to the transfer of aryl groups from mercuric salts to alkenes via palladium complexes.<sup>39</sup> A factor

common to arylation reactions described is that in the absence of an alkene biaryl derivatives are formed.

#### 4. MECHANISTIC INVESTIGATIONS

Since the discovery of the Wacker process there has been an upsurge of interest in reactions assisted by or catalysed by organometallic compounds, especially palladium compounds, many of these reactions being of synthetic and industrial importance. Unfortunately, elucidation of the mechanisms of these reactions has been slow. This is mainly because the processes involved are complex and thus a kinetic study, giving information about the rate-determining step, rarely gives information about what happens in the coordination sphere of the reactive complex, since this step is normally very fast. Also metal-catalysed reactions often give rise to a complex product distribution, thereby making an accurate materials balance difficult to achieve.

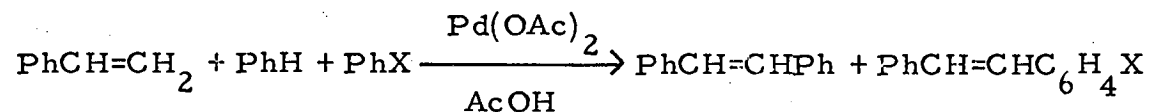
The first mechanistic investigations of the palladium acetate assisted arylation of alkenes were performed by Moritani,<sup>14-18, 24-29</sup> although Boyd,<sup>48</sup> Shue,<sup>42, 43</sup> and Norman<sup>44, 59, 60</sup> have made valuable observations.

The effect on the reaction of incorporation of substituents into the aromatic compound has been studied by Moritani<sup>15, 17</sup> and Boyd,<sup>48</sup> and of substituents into the alkene by Moritani,<sup>14, 16, 18, 24, 25, 28, 29</sup> Shue,<sup>42</sup> and Boyd.<sup>48</sup> Moritani has reviewed his mechanistic investigations<sup>61</sup> but, unaccountably, several results in the review are not in agreement with those published in an earlier paper.<sup>17</sup> Heck has reported the results of investigations into the mechanism of a related palladium-assisted arylation reaction.<sup>39, 40</sup>

##### 4.1 EFFECT OF SUBSTITUENTS IN AROMATIC COMPOUNDS

Both Boyd and Moritani chose styrene as the standard alkene, Moritani because of its known high reactivity in the reaction,<sup>15</sup> and Boyd in an attempt to clarify apparent inconsistencies in Moritani's

Table 2      The Competitive Reactions of Benzene and Monosubstituted Benzenes towards Styrene<sup>17</sup>



X	Yield (%) Stilbene	Yield (%) Substituted Stilbene	Isomer Distribution (%) <sup>*</sup>	Partial Rate Factor	Reactivity Ratio ( <sup>k</sup> X/ <sup>k</sup> H)
			<u>o</u> <u>m</u> <u>p</u>	<u>f</u> <u>o</u> <u>m</u> <u>p</u>	
CH <sub>3</sub>	36	26	3.8 0 96.2	0.083 <u>ca.</u> 0 4.17	0.72
C <sub>2</sub> H <sub>5</sub>	35	23	0 0 100	0 0 3.94	0.66
Cl	34	20	5 25 70	0.088 0.44 2.47	0.59
NO <sub>2</sub>	38	19	0 100 0	<u>ca.</u> 0 1.50 <u>ca.</u> 0	0.50

All reactions were carried out at 90°. All yields based on starting styrene.

In Moritani's report<sup>17</sup> some partial rate factors were incorrectly calculated.

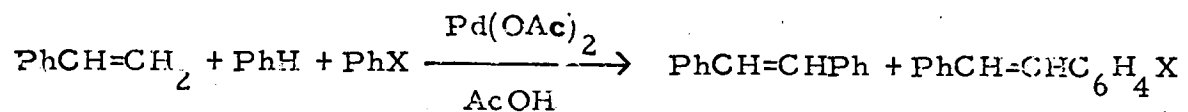
\* These figures not reported but were calculated from the percentage yield of each trans-substituted stilbene.

Table 3      The Competitive Reactions of Benzene and Monosubstituted Benzenes towards Styrene<sup>61</sup>

X	Isomer Distribution (%) <sup>*</sup>			Partial Rate Factors			Reactivity <sup>*</sup> Ratio ( $k_X/k_H$ )
	<u>o</u>	<u>m</u>	<u>p</u>	<u>f<sub>o</sub></u>	<u>f<sub>m</sub></u>	<u>f<sub>p</sub></u>	
CH <sub>3</sub>	24.3	31.5	44.2	1.56	2.02	5.68	2.14
C <sub>2</sub> H <sub>5</sub>	16.8	33.4	49.8	0.70	1.39	4.15	1.39
Cl	13.8	35.6	50.6	0.29	0.75	2.13	0.70
NO <sub>2</sub>	7.7	83.9	8.4	0.06	0.65	0.13	0.26
OCH <sub>3</sub>	36.5	5.4	58.2	5.65	0.83	18.04	5.17

\* These figures were not reported but were calculated from the given partial rate factors.

Table 4 Competitive Reactions of Benzene and Monosubstituted Benzenes with Styrene<sup>48</sup>



X	Reaction Temp °C	Yield (%)		Isomer Distribution (%)			Partial Rate Factors			Reactivity Ratio ( $k_X/k_H$ )
		Stilbene	Substituted Stilbene	<u>o</u>	<u>m</u>	<u>p</u>	$f_{\underline{o}}$	$f_{\underline{m}}$	$f_{\underline{p}}$	
CH <sub>3</sub>	94	22.1	35.3	27.9	72.1*		1.34	≤ 3.45	≤ 6.9	1.60
OCH <sub>3</sub>	100	20.1	51.4	35.8	5.75	58.5	2.75	0.44	9.00	2.56
NO <sub>2</sub>	99	36.7	3.50	14.9	77.7	7.40	0.04	0.22	0.04	0.095
CF <sub>3</sub>	93	38.2	6.90	1.40	80.4	18.2	0.0076	0.44	0.20	0.18

\* Total meta-plus-para isomers.

work. A series of competitive arylation reactions, in which a limited amount of styrene reacted with a large excess of an equimolar mixture of benzene and substituted benzene, was performed by each worker.<sup>17, 48</sup> The product mixture from such a reaction gives the following information: the overall reactivity of the two aromatic compounds (from the ratio of the yields of substituted products to unsubstituted products); and the relative reactivity of each site in the substituted benzene (partial rate factor,  $f_{ortho}$ ,  $f_{meta}$ , and  $f_{para}$ ). A partial rate factor is defined as the ratio of the reactivity of a specific site on the substituted benzene to the reactivity of a single site in unsubstituted benzene,<sup>62</sup> and is obtained by considering the isomer distribution of substituted products in conjunction with the amount of product derived from benzene.

Moritani's results have been published twice; in the original paper<sup>17</sup> and in a review,<sup>61</sup> and they are shown in Tables 2 and 3 respectively. Moritani claims the results published in the review<sup>61</sup> to be those published in the original communication,<sup>17</sup> but a comparison of Tables 2 and 3 shows Moritani's claim to be incorrect. There are other major discrepancies in supposedly identical results including the following: firstly, isomer distributions of products from reaction of styrene with mono-substituted benzenes are completely different in four of five cases; and secondly, in the original paper<sup>17</sup> Moritani states "..... if ethylbenzene and nitrobenzene ..... were allowed to react with styrene, both ethyl- and nitrostilbene were produced in the almost equal amounts." [27% nitrostilbene, 29% ethylstilbene], whereas in the review<sup>61</sup> he states "..... if ethylbenzene and nitrobenzene ..... are allowed to react with styrene, both nitro- and ethylstilbenes are produced in yields of 4.3% and 56%, respectively." No comment is made on these discrepancies nor on which set of results Moritani wishes to be accepted.

Because of these inconsistencies Boyd carried out competitive arylations,<sup>48</sup> repeating some of Moritani's work, and his results are shown in Table 4. Boyd's results are in reasonable accord with those published in Moritani's review<sup>61</sup> (Table 3) and thus it may be assumed that those in the original paper<sup>17</sup> are to be disregarded. From his

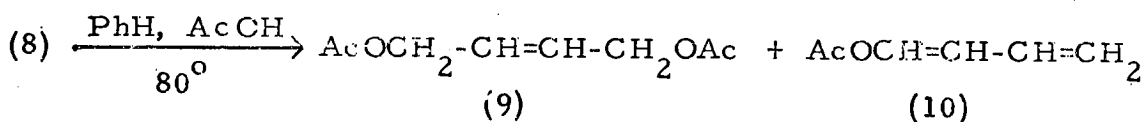
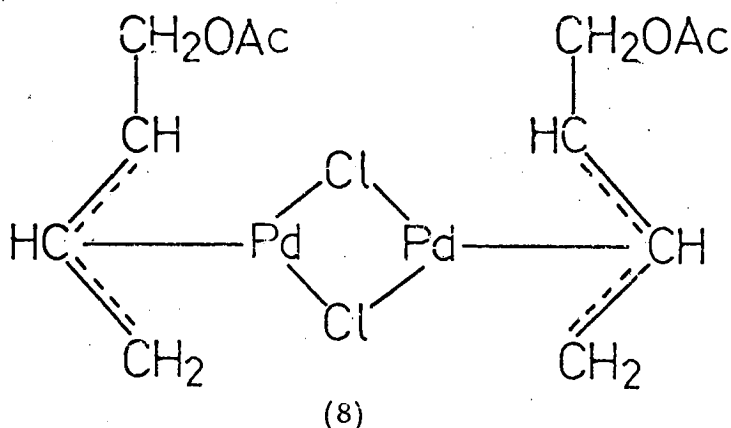
results, Boyd concluded that the observed isomer distribution is that which would be expected from an electrophilic aromatic substitution, although the reactivity of mono-substituted benzenes is influenced not so much by the substituent as it is in a typical electrophilic aromatic substitution, a conclusion with which Moritani now concurs.

The phenylation of styrene was investigated by Shue<sup>41-43</sup> who found a significant kinetic isotope effect, following the competitive reaction of benzene and hexadeuterobenzene.<sup>42</sup> From a reaction mixture containing styrene and an excess of an equimolar mixture of benzene and hexadeuterobenzene, a mixture of stilbene and penta-deuterostilbene was obtained in the ratio 5.3:1. From independent rate determinations a similar value was obtained.<sup>42</sup> These findings contradict Moritani's original conclusion,<sup>17</sup> that a substituent in the aromatic compound does not affect the reactivity, but is in agreement with both Moritani's more recent results<sup>61</sup> and those of Boyd<sup>48</sup> since an isotope effect of this size indicates that the aromatic species is involved in the rate-determining step of the reaction.<sup>63</sup>

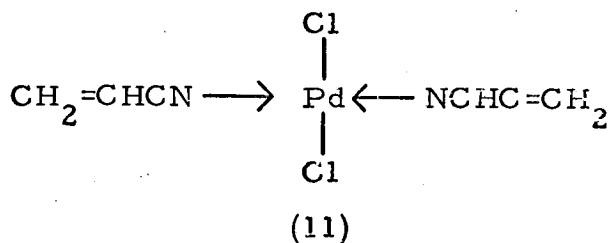
#### 4.2 EFFECT OF SUBSTITUENTS IN THE ALKENE

Moritani selected an assortment of substituted alkenes for investigation.<sup>16, 18</sup> In each case the products were derived by reaction of excess benzene with equimolar amounts of alkene and palladium acetate. Gaseous alkenes were bubbled through the reaction mixture at atmospheric pressure. The results obtained (Table 5) show clearly that phenylation, in many cases, is not the major reaction pathway; isomerisation, alkene coupling, acetoxylation, and acetoxylation with phenylation, being the main side-reactions. That both propene and buta-1, 3-diene undergo acetoxylation as the major reaction is, Moritani suggests,<sup>16</sup> due to the ease of formation of  $\pi$ -allyl complexes. Moritani<sup>16</sup> found that under the same reaction conditions a complex of this type,  $\mu$ -dichloro-bis ( $\pi$ -1-acetoxymethylallyl)palladium (II), (8) gave rise to the two products, 1,4-diacetoxymethylbut-2-ene (9) and 1-acetoxymethylbuta-1, 3-diene (10), formed in the attempted phenylation of butadiene.



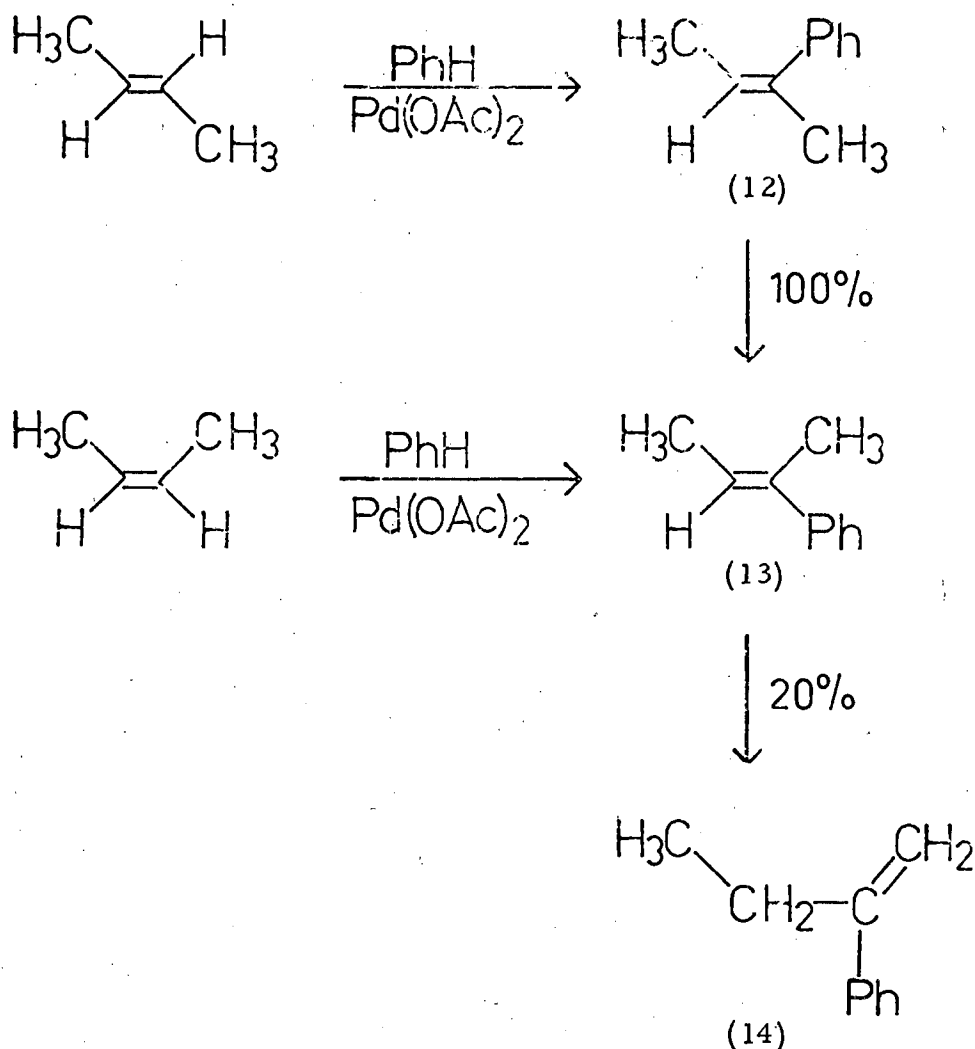


Alkenes containing polar groups, such as acrylonitrile, vinyl acetate and ethyl vinyl ether also give rise to product mixtures<sup>18</sup> (Table 5). Acrylonitrile shows lower reactivity towards phenylation than does styrene and this, it is suggested, may be due to the formation of an acrylonitrile-palladium acetate complex which would inhibit arylation by shielding the reaction site of palladium (II).<sup>18</sup> Acrylonitrile is known<sup>64</sup> to form a complex of this type (11) with palladium chloride.



dichloro-bis(acrylonitrile)palladium (II)

cis- and trans-But-2-ene give somewhat similar product distributions and this was explained by the observation that, under the reaction conditions, 2-phenyl-trans-but-2-ene (12), the expected product from trans-2-butene, isomerised quantitatively to the cis-isomer (13), and that the cis-isomer (13) isomerised, in 20% yield, to 2-phenylbut-1-ene (14), (Scheme 5).<sup>16</sup>



Scheme 5

Yamamura *et al.*<sup>65</sup> reported a similar isomerisation during investigation of the palladium acetate assisted phenylation of  $\beta$ -methyl- $\beta$ -nitrostyrene.

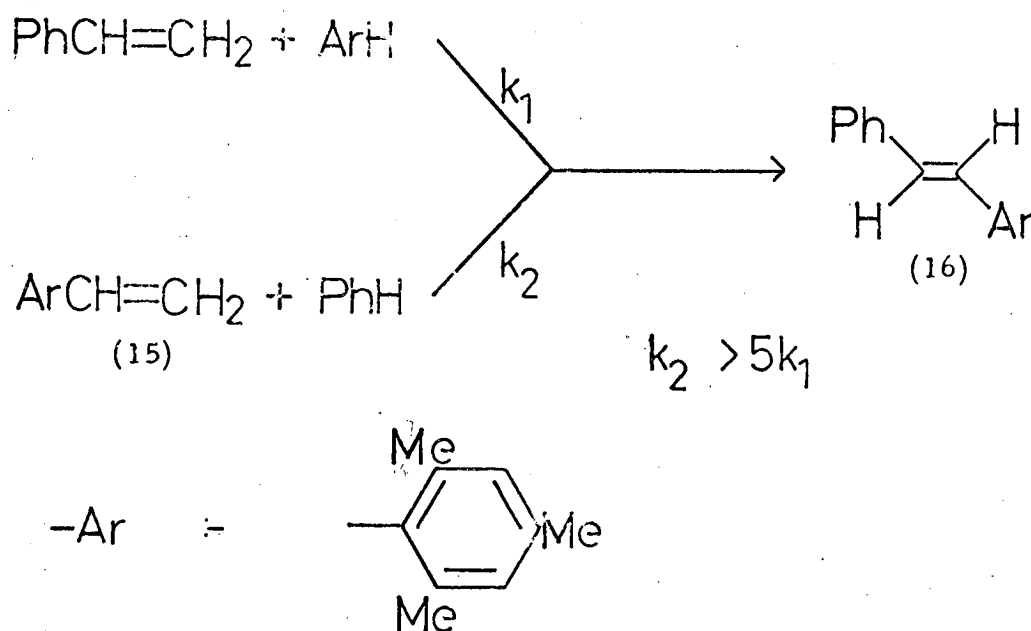
Although phenylation, acetoxylation, isomerisation and alkene coupling occurred both separately and together, to varying degrees, Moritani drew certain conclusions:

(i) the reactivity towards phenylation of simple lower alkenes decreases in the order, propene > trans-butene, cis-butene > but-1-ene, but alkenes which easily form  $\pi$ -allyl complexes give acetates and dimers as the major products.<sup>16</sup>

(ii) phenylation is enhanced by the presence of an electron-withdrawing group on the olefinic carbon atom, but this may be modified

by the ease with which a stable complex is formed with palladium,<sup>18</sup> such as is thought to occur with acrylonitrile and palladium acetate. Moritani then suggested that the reactivity of alkenes towards phenylation depends partly upon the ease with which the alkene forms a  $\pi$ -alkene complex with palladium (II).<sup>18</sup>

Recently Moritani published the results of investigations into the reaction of ortho-alkylstyrenes with benzene and of the reaction of styrene with alkylbenzenes.<sup>29</sup> One interesting result was that arylation of styrene with mesitylene occurred five times more slowly than did that of 2,4,6-trimethylstyrene (15) with benzene, both reactions giving the same product, 2,4,6-trimethyl-trans-stilbene, (16), (Scheme 6).



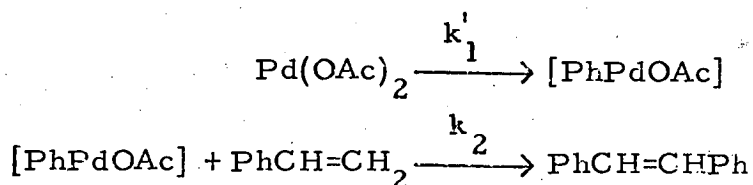
Scheme 6

From this, Moritani suggests that steric hindrance in the aromatic compound is more important than in the alkene.

Shue has studied the phenylation of styrene and  $\beta,\beta$ -dideuterostyrene,<sup>42</sup> both competitively and independently, and has found kinetic isotope effects of approximately 1 and 1.25 respectively. A value as low as 1.25 indicates a secondary kinetic isotope effect and so cleavage of the styrene- $\beta$ -hydrogen bond is not involved in the rate-determining step of the arylation.

Boyd performed kinetic studies of alkene arylation<sup>48</sup> in which

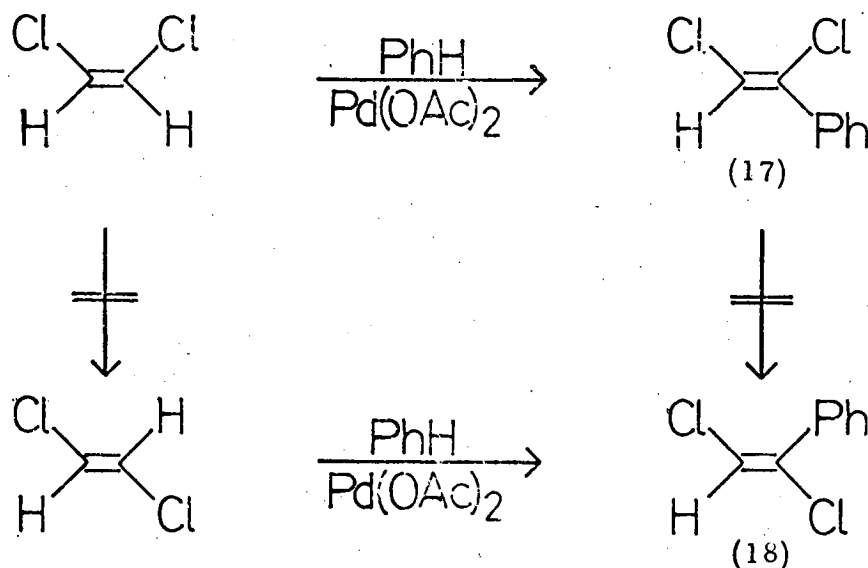
disappearance of the reactant alkene was determined and his results indicated a closer similarity to a first-order reaction than to a second-order reaction. Previous work led Boyd to support Shue's proposal that the rate-determining step of alkene arylation was palladium-aryl  $\sigma$ -bond formation, and a proposed reaction pathway, (Scheme 7), was simulated by use of an analogue computer.



Scheme 7

Because benzene is in vast excess the first step is pseudo-first order. The computer simulations matched kinetic results when  $k_2$  was greater than  $k_1$  by a factor of approximately 10 or more. This is, therefore, more evidence for reaction between palladium and the aromatic compound being the rate-determining step.

By use of alkenes which did not isomerise under the arylation conditions, Moritani investigated the stereochemistry of arylation.<sup>28</sup> Reaction of benzene with isomeric 1, 2-dichloroethylenes proceeded with complete retention of configuration, the products cis-1, 2-dichloro-1-phenylethylene (17) and its trans-isomer (18) having the same configuration as the respective reactant alkenes. Neither product is isomerised under the reaction conditions. (Scheme 8).

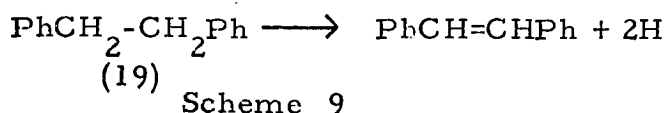
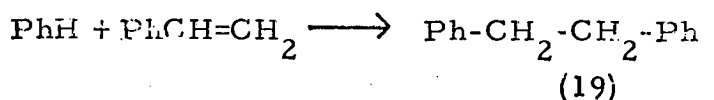


Scheme 8

Moritani infers, from these results, the existence of an alkene- $\sigma$ -bonded intermediate but a bridged, rigid or hindered intermediate, in which no rotation about the carbon-carbon bond can occur, is also possible.

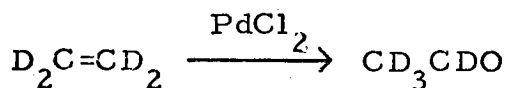
#### 4.3 OTHER OBSERVATIONS

A possible reaction path for alkene arylation is a stepwise addition-dehydrogenation. The reaction of styrene with benzene could thus be envisaged as shown in Scheme 9. Addition of the two reactant species affords bibenzyl (19) and its dehydrogenation gives stilbene.

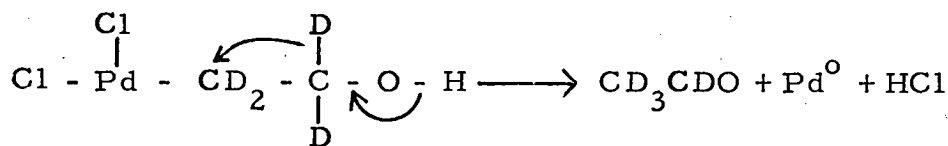


However, it was found that bibenzyl failed to dehydrogenate under the reaction conditions<sup>10, 12</sup> and so the intermediacy of bibenzyl was rejected.

Another possibility, which was later rejected, was a hydride shift, a step known to occur in the Wacker process.<sup>4</sup> Thus, if tetradeuteroethylene is oxidised by the Wacker process, no loss of deuterium in the product is found.

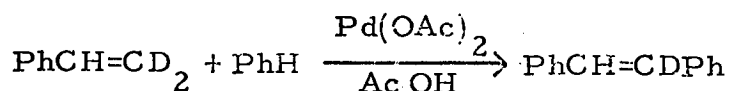


This is accounted for by a hydride shift step,<sup>66, 67</sup> in which a hydroxylated ethylene molecule,  $\sigma$ -bonded to palladium decomposes to products:



However, Moritani found, in his arylation reaction, that if  $\beta, \beta$ -dideuterostyrene was arylated with benzene the product contained

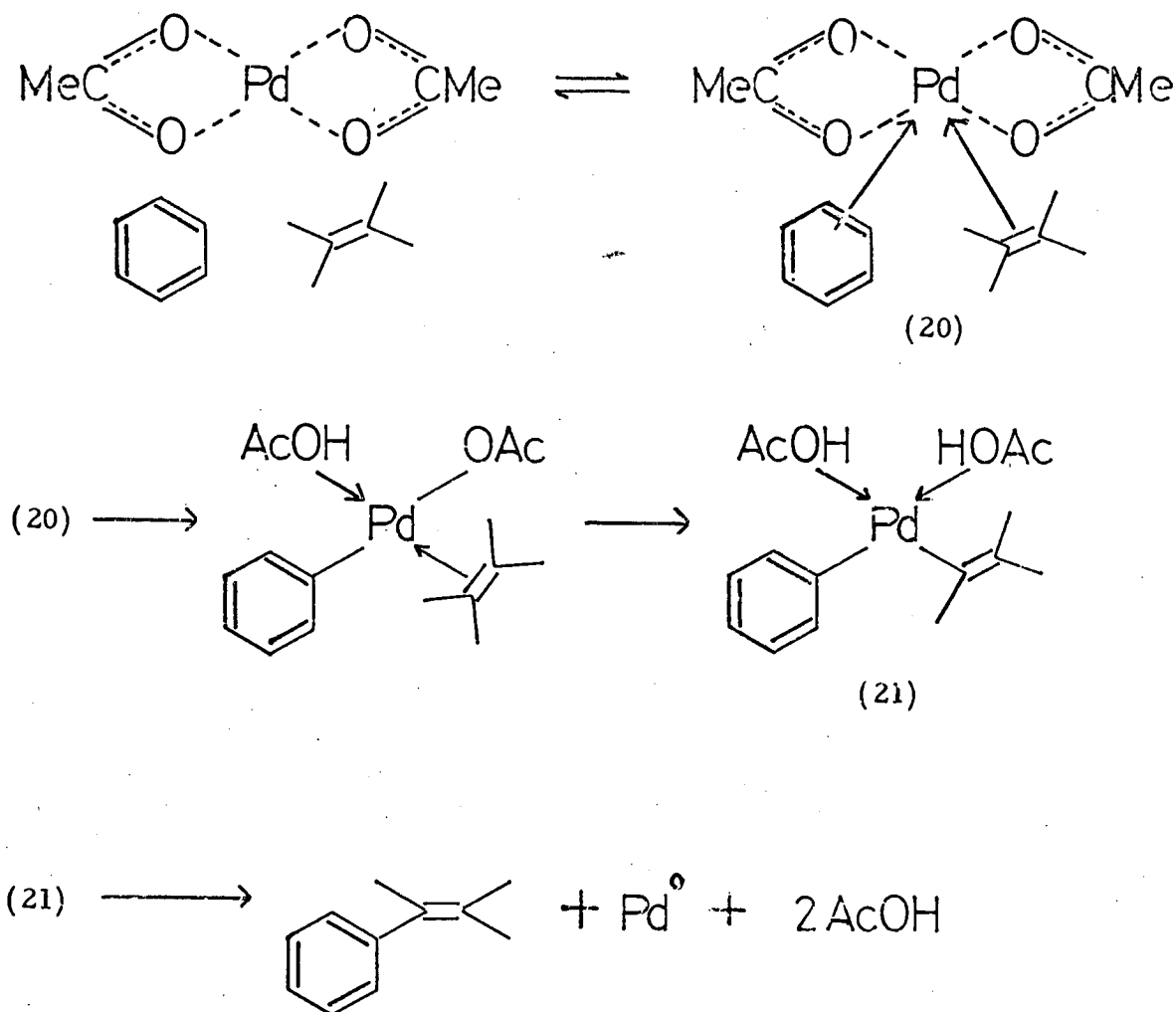
only one deuterium atom:<sup>24, 25</sup>



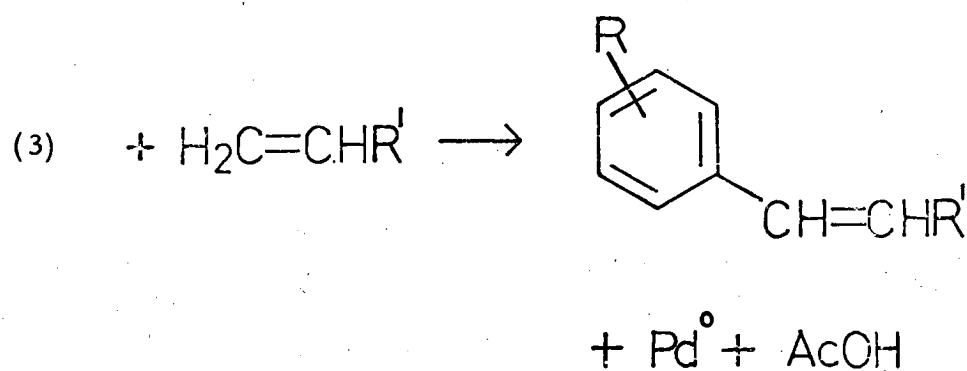
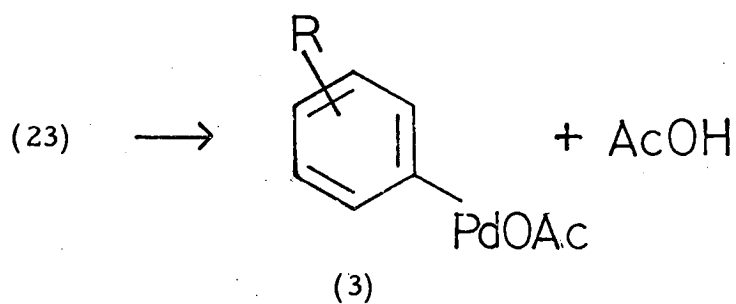
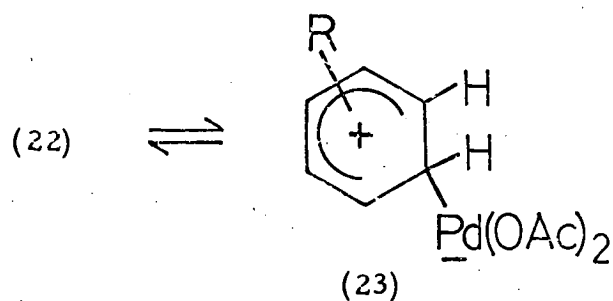
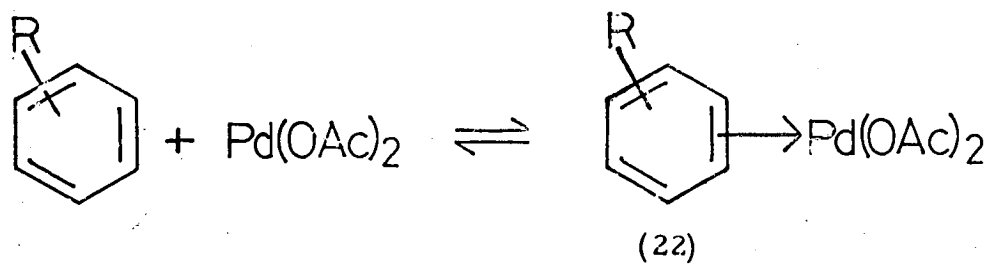
No hydride shift occurs and so in this respect, at least, the mechanism of alkene arylation differs from that of the Wacker process.

## 5. THE MECHANISM OF ALKENE ARYLATION

Moritani was the first worker to propose a reaction mechanism for palladium acetate assisted arylation of alkenes;<sup>18</sup> this mechanism is represented in Scheme 10. The alkene and aromatic compound both coordinate with palladium acetate to form the double  $\pi$ -complex (20).



Scheme 10



Scheme 11

The double  $\pi$  -complex (20) transforms in two steps to a palladium-alkene-aryl  $\sigma$  -complex (21), with proton transfer to acetate ligands. The  $\sigma$  -complex (21) then rapidly decomposes into phenylated alkene, acetic acid, and metallic palladium. Moritani postulates  $\sigma$  -bond formation between alkene and palladium to give (21) as the rate-determining step.<sup>18</sup> This was suggested on the basis of the variation of reactivity shown by substituted alkenes,<sup>16, 18</sup> and the lack of variation shown by aromatic compounds.<sup>17</sup> In his review, however, Moritani<sup>61</sup> suggests that the reaction proceeds via conversion of a  $\pi$  -arene- $\pi$  -alkene palladium complex to a  $\sigma$  -arene- $\sigma$  -alkene complex, without proposing a rate-determining step.

Shue's determination of kinetic isotope effects tends to disprove Moritani's idea. Loss of hydrogen from the alkene as the slow step is discounted and, instead, hydrogen loss from the aromatic compound is proposed as being rate-determining.<sup>42</sup>

Reversible  $\sigma$  -bond formation between palladium and the aromatic compound is ruled out because, after reaction of styrene with benzene- $d_0$  and benzene- $d_6$ , no isotopic scrambling was found, only benzene- $d_0$  and benzene- $d_6$  being present in the product mixture.

Based on his own work and evidence relating to this and allied reactions, Boyd<sup>48</sup> proposed a series of steps for alkene arylation (Scheme 11).

The first step is reversible formation of a palladium- $\pi$  -complex (22), from palladium acetate and the aromatic compound. Subsequent aryl-carbon to palladium  $\sigma$  -bond formation gives (23). The zwitterionic species (23) then undergoes non-reversible rate-determining loss of a proton from the aromatic ring, and of an acetate group from palladium to form the  $\sigma$  -aryl-palladium acetate (3) which then reacts with the alkene in a fast step for which a mechanism has been proposed.<sup>39, 59</sup> [Introduction Section 3].

That this mechanism (Scheme 11) can account for product distribution<sup>48, 61</sup>, partial rate factors observed in competitive arylation reactions<sup>48, 61</sup>, and the kinetic isotope effects observed by Shue<sup>42</sup> will be demonstrated later.



## 6. PROGRAMME OF WORK

The preceding sections show that mechanisms for the palladium (II) acetate assisted arylation of alkenes have been proposed by Moritani<sup>18</sup> and Boyd.<sup>48</sup> It was considered, however, that further investigations were necessary because some of Moritani's results were anomalous and because Boyd had observed batch effects with palladium acetate which he had not investigated further.

In common with Moritani and Boyd, styrene was chosen as the alkene because of its known high reactivity towards arylation<sup>15</sup> but other alkenes were occasionally used. Initially the work was concerned with the preparation and purification of palladium acetate in order to eliminate the known batch effects. Thereafter attention was turned towards elucidation of the mechanism of alkene arylation. To this end substituted benzenes and ring-substituted styrenes were used to determine the effect of the substituent on the arylation reaction. The use of techniques other than gas-liquid chromatography to study the reaction was investigated.

Alkene arylations assisted by palladium (II) compounds other than palladium acetate were performed. Some alkene cyclisation reactions were also attempted.

## EXPERIMENTAL

EXPERIMENTAL: CONTENTS

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# 1 INSTRUMENTATION AND TECHNIQUES

## Gas Liquid Chromatography (g.l.c.)

For analytical and quantitative gas liquid chromatographic investigations, a Pye 104 Model 54 Chromatograph, fitted with a Pye Wide Range amplifier, was used together with 2m x 3mm i. d. packed columns. The following stationary phases, supported on acid-washed silanised 80-100 mesh Chromosorb G, were employed: neopentylglycol succinate, 2.5% loading, (2.5% NPGS); silicone elastomer E 301, 1% loading, (1% SE30) and polyethyleneglycol (m.w. 20,000), 5% loading, (5% CAR 20M). Nitrogen carrier gas was used at 50 ml min<sup>-1</sup>. Gas supplies to the flame ionisation detector were hydrogen (50 ml min<sup>-1</sup>) and air (750 ml min<sup>-1</sup>). For quantitative work, gas flows were carefully checked and the detector maintained at 280° by the detector oven. Integration of the chromatograms was carried out using a Kent Chromalog 2 automatic electronic integrator and, latterly, a Hewlett-Packard Model 3373B automatic electronic integrator.

## Quantitative Methods and Data Treatment

Due to the unique response of the flame ionisation detector, calibration of the Pye 104 instrument was necessary. The peak area ratio of the standard to the compound to be measured was calculated from the integrator print-out, and the molar ratio corresponding to this was obtained from a calibration graph. This graph of molar ratio versus peak area ratio was obtained from the analysis of standard mixtures of the two pure compounds concerned. In all cases, the graph was found to be a straight line passing through, or very close to, the origin. In several cases, due to faults in the integrator, peak areas were obtained by a simple calculation,<sup>68</sup> integration being carried out by direct peak area measurement, (peak height x peak width at half height).

Calculations were carried out using a Wang 360K electronic calculator and CP-2M programme card reader, and a Sumlock Compucorp 340 Statistician electronic calculator, both calculators allowing straight-line fitting by the method of least squares to be carried out quickly and thus, routinely. All calibration graph data were treated in this way. Molar ratios were thus available by calculation, thereby eliminating the inconsistencies inherent in graph reading.

The reproducibility of the peak area ratios obtained under optimum conditions from the chromatogram-integrator combination was found to be within the manufacturers' specification of 0.2%. However, conditions were not always at the optimum<sup>69</sup> and for this reason a pair of peak area ratios were said to be concordant if their difference was less than 2% of the smaller figure. The reasons for the discrepancies which arose were two-fold. Firstly, small quantities of involatile materials with long retention times, arising from previous injections, were added into peaks of interest by the integrator. This problem could be eliminated either by careful timing of injections or by purging the column after each injection or every few injections. Both these procedures were costly in terms of time and this factor had to be balanced against the likely improvement in reproducibility which would be obtained. Secondly, the integrator had a limited capability to deal with grossly distorted peaks and even perfectly Gaussian-shaped peaks gave erroneous integrals in cases of severe overlapping produced because of imperfect separations. By adjusting g.l.c. conditions, these errors could be minimised.

Measurements on reaction mixtures usually produced ratios which were reproducible within the instrument specification. Those measurements which were disregarded were those that were dubious from the point of view of either the recorder trace or the integrator print-out or both. Satisfactory ratios within the 2% concordance limit were averaged for use in each case.

### Column Chromatography

Alumina used for column chromatography was Laporte

Industries Ltd. activated aluminium oxide, type H. It was found to be of activity 1 (Brockmann scale<sup>70</sup>).

Alumina for dry column chromatography (d.c.c.) was prepared from chromatographic alumina treated with indicator (Woelm Fluorescent Indicator Green added to the adsorbent, 0.5%) for short wave u.v. (254 nm) and deactivated to Brockmann activity 3 as described by Loev and Goodman.<sup>70</sup>

### Thin Layer Chromatography

Thin layer chromatograms were obtained on 0.3mm layers of alumina (Merck, aluminium oxide G). Components in the developed chromatograms were detected either by their own fluorescence in u.v. light or by their quenching of the fluorescence of added indicator and, in any case, by their reaction with iodine.

### Nuclear Magnetic Resonance Spectroscopy (n.m.r.)

Spectra were recorded on a Varian EM 360 spectrometer which operated at a frequency of 60 MHz. Variable temperature studies were recorded using a Varian HA-100 instrument operating at 100 MHz. Chemical shifts were recorded as tau ( $\tau$ ) values in parts per million using tetramethylsilane as internal standard ( $\tau = 10.0$ ). Spectra were recorded in 10-15% w/v solutions.

### Mass Spectroscopy (m.s.)

Mass spectra were recorded at 70eV, unless otherwise stated, on an A.E.I. MS 902 double focusing spectrometer and on a V.G. Micromass 12, single focusing mass spectrometer. Reaction mixtures were analysed using either an A.E.I. MS 20 mass spectrometer or the V.G. Micromass 12, coupled to a Pye 104 gas chromatograph (g.l.c./m.s.) using helium as the carrier gas. Spectra were counted either by hand or by computer (Digital PDP 11).

### Infrared Spectroscopy (i. r.)

Infrared spectra were obtained using a Perkin-Elmer 157G spectrophotometer. Samples were examined either as liquid films or Nujol mulls between sodium chloride plates.

### Ultraviolet Spectroscopy (u. v.)

Ultraviolet spectra were recorded on a Unicam SP800 instrument using a matched pair of 1.0 cm quartz cells.

### Elemental Analysis

Microanalyses were carried out on a Perkin-Elmer Elemental Analyser 240 by Mr. J. Grunbaum, Department of Chemistry, University of Edinburgh.

### Solvents and Reagents

Chromatographic solvents were dried before use, hydrocarbons and ether with sodium; chlorinated solvents with magnesium sulphate and then molecular sieve (Linde type 4A). Light petroleum (b. p. 40-60° unless otherwise stated) was always distilled before drying. Benzene was purified by distillation of the sodium dried solvent from calcium hydride in an atmosphere of nitrogen and was stored over molecular sieve. Glacial acetic acid was purified by the method of Eichelberger and La Mer.<sup>71</sup> Reagent grade glacial acetic acid was heated under reflux for 0.5 h with potassium permanganate (2% w/w) and was then distilled. The purified acid was heated under reflux with triacetyl borate and then carefully distilled. The purity of all reagents was estimated before use, generally by g.l.c., and if necessary they were recrystallised or fractionally distilled. Reagents for competition reactions and kinetic experiments were distilled and stored over molecular sieve. Toluene was treated with concentrated sulphuric acid and distilled as described by Vogel.<sup>72</sup> Molecular sieve was dried at 310° and stored in a desiccator.



## 2. PREPARATION OF PALLADIUM COMPOUNDS

### 2.1 Palladium Acetate

2.1 (i) Preparation. Palladium acetate was prepared many times, by one basic method. However, modifications of this method were sometimes used.

Method (a). Palladium acetate was prepared from palladium sponge as described by Wilkinson et al.<sup>73</sup>

Palladium chloride (5.0 g, 28.2 mmol) was added slowly with stirring to hydrazine hydrate (15.0 g, 300 mmol). Fumes of hydrogen chloride were evolved vigorously and the mixture became warm. When the addition was complete the mixture was allowed to cool and palladium sponge (3.0 g, 28.2 mmol, 100% yield) was removed by filtration and washed thoroughly with water, acetone and ether. After drying by suction, palladium sponge (2.6 g, 24.4 mmol) was added to a mixture of glacial acetic acid (175 ml, 3.6 mol, excess) and concentrated nitric acid (1.8 ml) and the mixture was heated under reflux until no more brown fumes of nitrogen dioxide were evolved. The remainder of the palladium sponge (400 mg, 3.8 mmol) was then added and the mixture boiled again until no more brown fumes were evolved. The solution was filtered hot to remove unreacted palladium (ca. 500 mg) and was then allowed to cool. The precipitated palladium acetate (ca. 2 g, 89 mmol, 31%) was collected and dried for 3 h under high vacuum. The mother liquor was retained.

Method (b). As method (a) except that mother liquors from previous palladium acetate preparations were used instead of glacial acetic acid.

Method (c). As method (a) except that when no more brown fumes of nitrogen dioxide were evolved, the mixture was heated under reflux for a further 20 min.

## 2.1 (ii) Purification.

Method I. Palladium acetate prepared by method (a) was recrystallised from benzene.

Method II. Palladium acetate prepared by method (a) was dissolved in warm benzene, the solution being mixed with half its volume of glacial acetic acid, and the benzene was allowed to evaporate slowly at room temperature. The acetate precipitated and was recovered from the solution.

Method III. Palladium acetate prepared by method (a) was washed with cold light petroleum and was dried over phosphorus pentoxide at 50° under high vacuum for 3 h.

Method IV. This purification was performed by the method of Davidson.<sup>74</sup> Palladium acetate (3 g, 13.4 mmol), prepared by method (a), was ground to a fine powder and was worked into a paste with concentrated sulphuric acid (3 ml). The paste was heated to 135° for 40 min, the paste then being brown with grey specks of palladium metal. The paste was cooled, dissolved in water (50 ml), and sodium carbonate was added in small portions. After addition of sodium carbonate (ca.4.5 g) some precipitation occurred. Glacial acetic acid (5 ml) was added and a small crop of palladium acetate was removed by filtration. Sodium carbonate (ca.0.5 g) was added followed by addition of acetic acid (15 ml), after which palladium acetate precipitated.

Difficulties, however, were encountered using this method. Firstly, in two cases no precipitation occurred and, secondly, in two cases precipitation of a reddish-brown solid occurred which was not palladium acetate. Davidson has also encountered similar difficulties.

Method V. Palladium acetate prepared by method (c) was dissolved in glacial acetic acid and air was bubbled through the solution

### Key

A - amorphous solid; B - brown; C - crystals;

O - orange-brown; P - purple; R - reddish brown;

e - palladium acetate prepared by Engelhard Industries Inc.

\* - palladium acetate prepared in previous experiments.

a, b, and c - refer to the corresponding method in the text.

I to VI - refer to the corresponding method in the text.

1, 2 - refer to the crop of material recovered.

$\omega_1$ ,  $\omega_2$  and  $\omega_3$  - refer to (COO) antisymmetric stretch, (COO) symmetric stretch, and (COO) deformation respectively.

Note i) Where no entry is made for nitrogen in the elemental analysis, no analysis was performed.

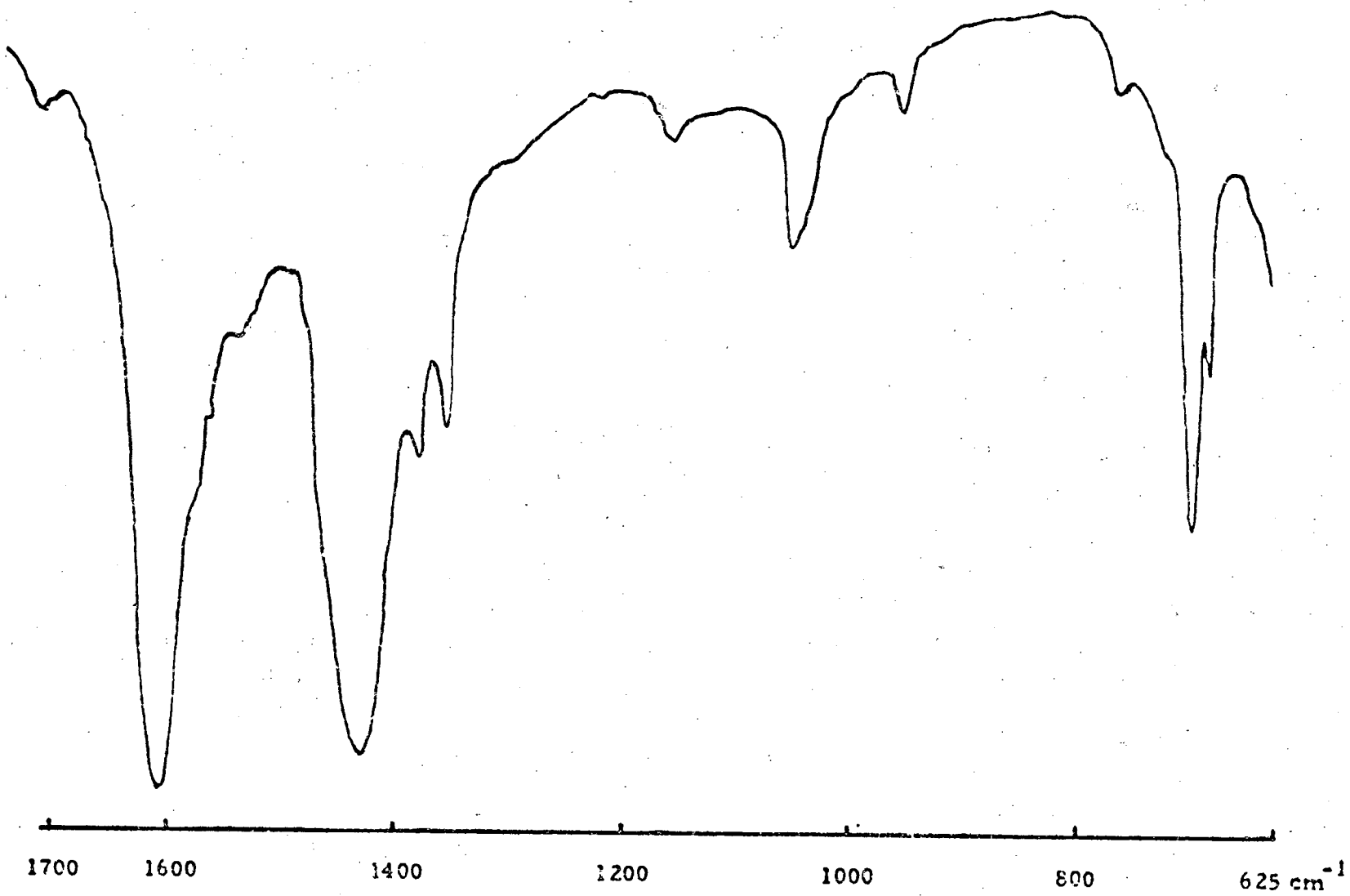
ii)  $\text{Pd}(\text{OAc})_2$  Batch 1 was prepared by Dr. J.M. Davidson and was purified by his method (IV).

Figure 1a



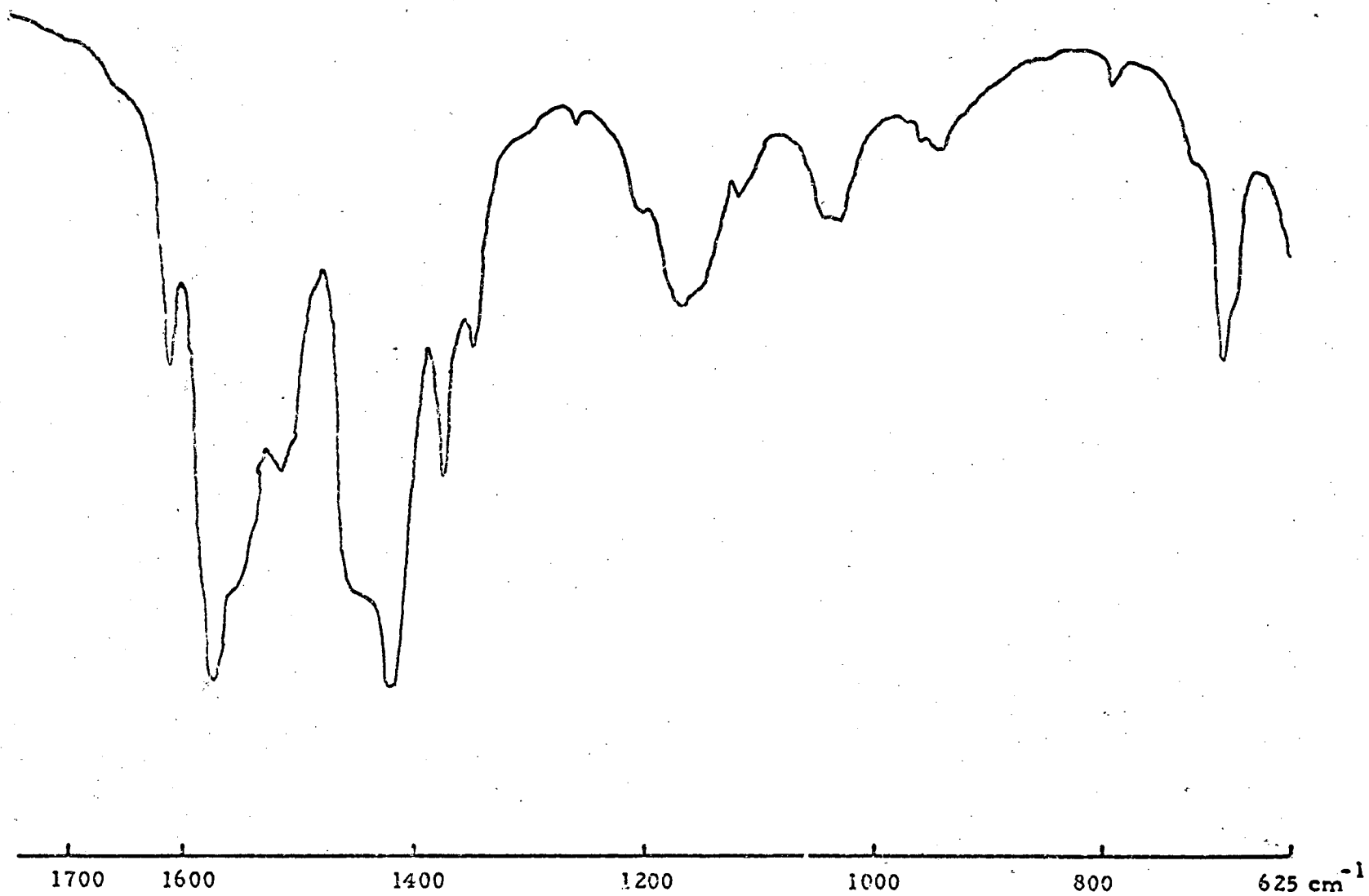
I.r. Spectrum of Palladium Acetate Batch 1

Figure 1b



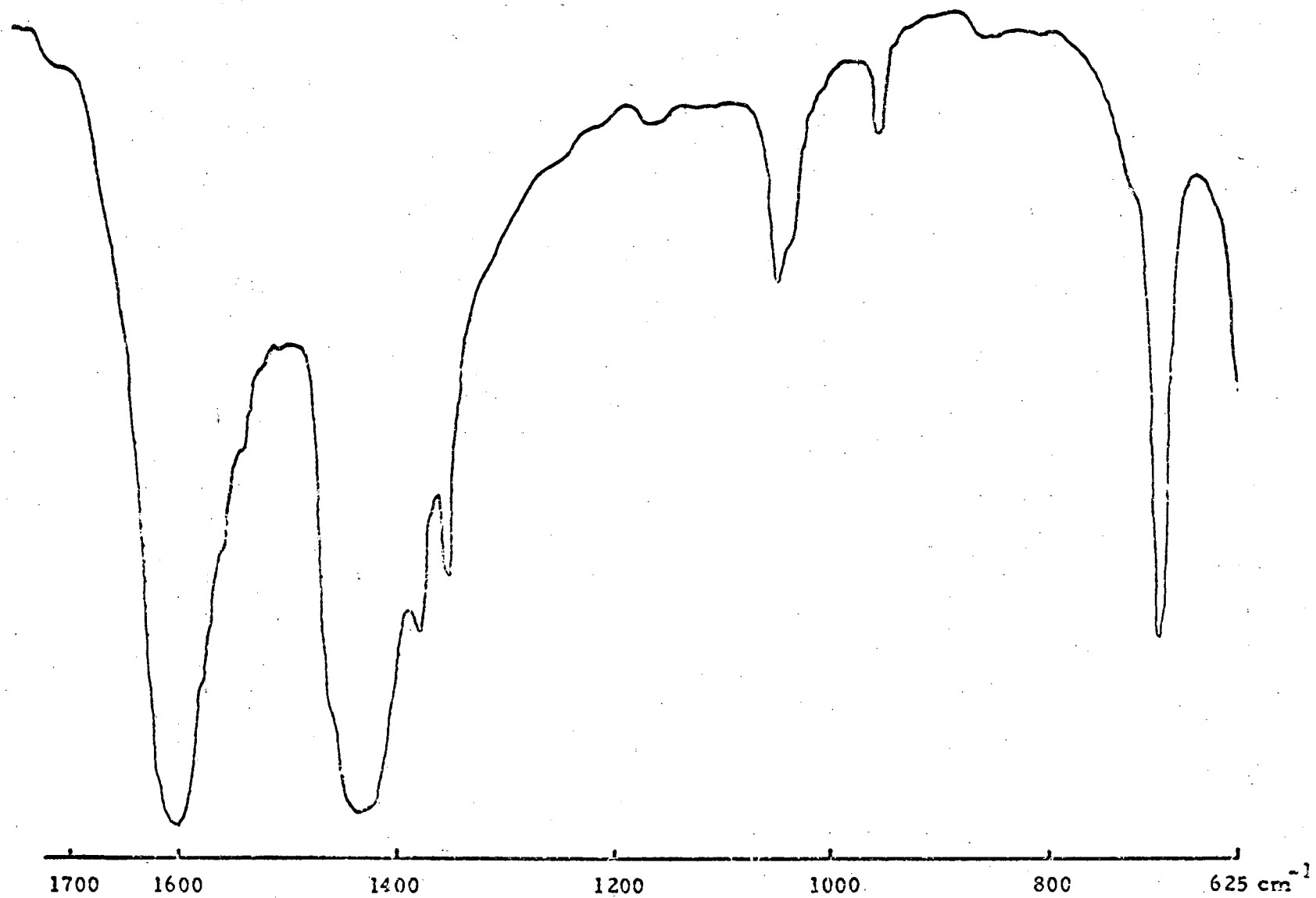
I. r. Spectrum of Palladium Acetate Batch 5B

Figure 1c



I. r. Spectrum of Palladium Acetate Batch 9A

Figure 1d



I. r. Spectrum of Palladium Acetate Batch 11

which was heated under reflux for 2 h. The acetate precipitated from the cooling solution.

Method VI. Palladium acetate, supplied by Engelhard Industries Inc., was recrystallised from glacial acetic acid.

Physical data of all batches of palladium acetate are listed in Table 6. The i. r. spectra of four batches of palladium acetate, chosen to illustrate their differences in the region  $1700\text{ cm}^{-1}$  to  $625\text{ cm}^{-1}$ , are shown in Figure 1.

## 2.2 Palladium Propionate

This was prepared from palladium sponge and propionic acid by the method of Wilkinson,<sup>73</sup> which is identical to the preparation of palladium acetate. The propionate was recovered as light-brown crystals (4.5 g, 63%), m. p.  $154^{\circ}$  (lit.,<sup>73</sup>  $161-165^{\circ}$ ),  $\nu_{\text{max}}$  1603 and  $1472\text{ (COO)}\text{ cm}^{-1}$ ,

Found: C, 27.94; H, 3.96; N, 0.35%.

Calc. for  $\text{C}_6\text{H}_{10}\text{O}_4\text{Pd}$ : C, 28.54; H, 3.99; N, 0.00%.

## 2.3 Palladium Benzoate

This was prepared by the method of Wilkinson.<sup>73</sup> A benzene solution (170 ml) of palladium acetate (1.00 g, 4.47 mmol) and benzoic acid (1.65g, 13.51 mmol) was evaporated on a steam-bath to give a brown-black solid. This residue was washed with ether (100 ml) to remove benzoic acid. Recrystallisation afforded yellow - brown crystals of the benzoate (0.55 g, 36%), m. p.  $220^{\circ}$  (decomp.) (benzene), [lit.,<sup>73</sup>  $220^{\circ}$  (decomp.)],  $\nu_{\text{max}}$  1613 and  $1405\text{ (COO)}\text{ cm}^{-1}$ ,

Found: C, 50.48; H, 3.27; N, 0.00%.

Calc. for  $\text{C}_{14}\text{H}_{10}\text{O}_4\text{Pd}$ : C, 48.19; H, 2.89; N, 0.00%.

## 2.4 Dichlorobis(benzonitrile)palladium (II)

The method of Kharasch<sup>50</sup> was used. Palladium chloride (4 g, 22.6 mmol) in benzonitrile (135 ml) was heated on a steam-bath



but not all the palladium chloride dissolved. The undissolved palladium chloride (ca. 1 g) was collected and the filtrate on cooling gave a yellow precipitate. More precipitate was obtained on addition of light petroleum (25 ml).

The recovered palladium chloride was dissolved in hot benzonitrile (100 ml) and the solution filtered and cooled. The identical work-up to before afforded more precipitate. The combined precipitates were washed with cold light petroleum (200 ml) and were dried under high vacuum for 4 h to give dichlorobis(benzonitrile) palladium, a yellow solid, (4.7 g, 54%), m.p. 127° (decomp.),  $\nu_{\text{max.}}$  2295 (C≡N) cm<sup>-1</sup>,

Found: C, 44.10; H, 2.61; N, 7.61%.

Calc. for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>Pd: C, 43.84; H, 2.63; N, 7.30%.

### 3. PREPARATION OF SUBSTITUTED STILBENES

#### 3.1 3-Chloro-trans-stilbene

This compound was prepared by a Wittig reaction.<sup>75,76</sup>

Benzyltriphenylphosphonium chloride was prepared by heating a mixture of benzyl chloride (38.0 g, 0.3 mol) and triphenylphosphine (79.0 g, 0.3 mol) in dimethylformamide (90 ml) until all the triphenylphosphine dissolved. The solution became cloudy as the product precipitated. After filtering, washing and drying, the salt was obtained (105.0 g, 90%).

Methanolic sodium methoxide, prepared by the addition of sodium (1.0 g, 0.044 mol) to A.R. methanol (200 ml), was added over a few minutes to a solution of 3-chlorobenzaldehyde (4.3 g, 0.029 mol) and benzyltriphenylphosphonium chloride (11.7 g, 0.03 mol) in A.R. methanol (75 ml). The mixture was then heated under reflux for 16 h. After removal of solvent, the residue was extracted with chloroform and water, the combined organic washings were dried over anhydrous magnesium sulphate and the chloroform removed under reduced pressure. The residue which contained both cis and trans isomers was heated under reflux for 2.5 h in nitrobenzene (35 ml) with a crystal of iodine. Nitrobenzene was removed by distillation in vacuo. Triphenylphosphine oxide and remaining nitrobenzene were removed by d.c.c. using light petroleum as eluant. A white solid (3.6 g) was recovered and was recrystallised to give 3-chloro-trans-stilbene as white crystals (3.0 g, 46%), m.p. 73° (light petroleum) (lit.,<sup>77</sup> 74°),  $\nu_{\text{max}}$  970 (:CH)  $\text{cm}^{-1}$ ,  $\tau$  [CDCl<sub>3</sub>] 2.57-2.95 (m, 9H, ArH) and 3.00 (2H, s, :CH).

#### 3.2 4-Chloro-trans-stilbene

The method for 3-chloro-trans-stilbene was used to give the product 4-chloro-trans-stilbene as white crystals (2.2 g, 34%), m.p. 129° (methanol) (lit.,<sup>77</sup> 129°),  $\nu_{\text{max}}$  970 (:CH)  $\text{cm}^{-1}$ ,  $\tau$  [CDCl<sub>3</sub>] 2.44-2.90 (m, 9H, ArH) and 3.00 (s, 2H, :CH).

### 3.3 2, 5-Dimethyl-trans-stilbene

2, 5-Dimethylbenzaldehyde was prepared as described by Jolad and Rajagopal.<sup>78</sup>

A mixture of paraformaldehyde (11.5 g, 0.38 mol), hydroxylamine hydrochloride (26.3 g, 0.38 mol) and water (170 ml) was maintained at 40° until a clear solution was obtained. Hydrated sodium acetate (51 g, 0.38 mol) was added and gentle heating under reflux for 15 min gave a 10% aqueous solution of formaldoxime.

Meanwhile, concentrated hydrochloric acid (57 ml) was added slowly to a stirred mixture of 2, 5-dimethylaniline (30.3 g, 0.25 mol) in water (50 ml). The reaction mixture was cooled to room temperature, ice (100 g) was added and the temperature was maintained between -5° and +5° (ice-salt bath). A solution of sodium nitrite (17.5 g, 0.25 mol) in water (25 ml) was added dropwise with stirring to the reaction mixture and, when the addition was complete, stirring was continued for 15 min. The red solution of the diazonium salt was made neutral to Congo red paper by addition of a solution of hydrated sodium acetate (22 g) in water (35 ml).

A solution of hydrated cupric sulphate (6.5 g, 0.026 mol), sodium sulphite (1.0 g, 0.008 mol) and hydrated sodium acetate (160 g, 1.17 mol) in water (180 ml) was added to the 10% aqueous solution of formaldoxime. The neutral aqueous solution of the diazonium salt was introduced below the surface of the formaldoxime solution, the temperature being kept at 10-15°. On completion of the addition the reaction mixture was stirred for a further 1 h and was then treated with concentrated hydrochloric acid (230 ml) and was heated under reflux for 2 h.

The resultant mixture was steam-distilled and the distillate (ca. 1 l.) was saturated with sodium chloride and was extracted with ether (3 x 150 ml). The combined ethereal extracts were washed with saturated aqueous sodium chloride (3 x 20 ml), 10% w/v aqueous sodium hydrogen carbonate (3 x 20 ml) and again with saturated aqueous sodium chloride (3 x 20 ml). Evaporation of the ether under

reduced pressure gave the crude 2,5-dimethylbenzaldehyde as a yellow liquid to which was added, with cooling, 40% w/v aqueous sodium metabisulphite (90 ml) previously heated to 60°. The mixture was shaken for 1 h and left for 12 h. The solid bisulphite addition compound was collected, washed with ether (2 x 70 ml) and was then heated under reflux for 2 h with concentrated sulphuric acid (40 ml) and water (200 ml). The cooled reaction mixture was extracted with ether (3 x 100 ml). The ether extract was washed with saturated aqueous sodium chloride solution, was dried over anhydrous sodium sulphate and was evaporated under reduced pressure. The residual oil was distilled in vacuo to afford the pure 2,5-dimethylbenzaldehyde as a pale yellow liquid (11.0 g, 32%), b.p. 104°/14 mm (lit.,<sup>79</sup> 58-59°/1.0 mm),  $\nu_{\text{max.}}$  3020, 2950, 2860 (CH), 2720 (CH) and 1675 (CO) cm<sup>-1</sup>, identical with an authentic sample.

2,5-Dimethyl-trans-stilbene was prepared from 2,5-dimethylbenzaldehyde by a Wittig reaction. A methanolic solution of sodium methoxide, prepared by adding sodium (2.3 g, 0.10 mol) to A.R. methanol (200 ml), was added over a few minutes to a solution of 2,5-dimethylbenzaldehyde (9.5 g, 0.07 mol) and benzyltriphenylphosphonium chloride (27.6 g, 0.07 mol) in A.R. methanol (75 ml). The mixture was heated under reflux for 16 h. After removal of solvent the residue, a brown oil, was extracted with chloroform and water, the organic layer then being dried over anhydrous magnesium sulphate and the solvent removed. The residue which contained a mixture of the cis- and trans-stilbenes and triphenylphosphine oxide was heated under reflux for 50.5 h in light petroleum (b.p. 60-80°) with a crystal of iodine. After 26.5 h, triphenylphosphine oxide was removed by d.c.c. with light petroleum as eluant, and the alkene mixture analysed by g.l.c. (2 m, 2.5% NPGS, 200°). After 50.5 h, purification by d.c.c. and crystallisation gave 2,5-dimethyl-trans-stilbene as white needles, (3.9 g, 25%), m.p. 42° (n-hexane) (lit.,<sup>15</sup> 43-44°),  $\nu_{\text{max.}}$  965 (:CH) cm<sup>-1</sup>,  $\tau$  [CDCl<sub>3</sub>] 2.55-3.10 (m, 8H, ArH; 2H, :CH) and 7.63 (s, 6H, Me).

### 3.4 1-(4-Chlorophenyl)-1,2-diphenylethylene

1-(4-Chlorophenyl)-1,2-diphenylethanol was prepared by a Grignard reaction. A solution of benzyl chloride (21.1 g, 0.17 mol) in anhydrous ether (75 ml) was added slowly to dry magnesium (4.1 g, 0.17 mol) and a crystal of iodine in anhydrous ether (30 ml). The mixture was heated gently to start the reaction and the rate of the reaction was controlled by cooling (ice-bath). When the addition was complete, the reaction was heated under reflux for 0.5 h.

A solution of 4-chlorobenzophenone (36.1 g, 0.17 mol) in anhydrous ether (300 ml) was added slowly with stirring to the solution containing the Grignard reagent giving an immediate red coloration. The rate of the reaction was controlled by cooling (ice-bath) and when the addition was complete the reaction mixture was stirred for 1.5 h. Addition of aqueous ammonium chloride (50 g/150 ml) gave incomplete separation of the ethereal and aqueous phases but addition of 2N hydrochloric acid (150 ml) did give complete separation, the organic layer being yellow. The aqueous phase was washed with ether (3 x 200 ml). The combined washings and ethereal phase were washed with saturated aqueous sodium hydrogen carbonate (3 x 200 ml) and water (3 x 200 ml) and were then dried over anhydrous magnesium sulphate. Evaporation of the ether under reduced pressure and crystallisation of the residue gave the product as a cream solid (32.3 g, 62%), m.p.  $80^{\circ}$  [light petroleum (b.p.  $60-80^{\circ}$ )/ethanol],  $\nu_{\text{max.}}$  3565 (OH)  $\text{cm}^{-1}$ ,  $\tau$  [ $\text{CDCl}_3$ ] 2.50-3.33 (m, 14H, ArH; 1H, OH) and 6.40 (s, 2H,  $\text{CH}_2$ ),

Found: C, 78.08; H, 5.76%.

Calc. for  $\text{C}_{20}\text{H}_{17}\text{ClO}$ : C, 77.80; H, 5.50%.

1-(4-Chlorophenyl)-1,2-diphenylethylene. The cis- and trans-isomers were prepared by dehydration of the carbinol. 1-(4-Chlorophenyl)-1,2-diphenylethanol (2 g, 6.5 mmol) was dehydrated by distilling over 20% sulphuric acid (1 drop) under high vacuum. A colourless oil (1.2 g, 60%), b.p.  $162^{\circ}/0.4$  mm was collected which solidified on cooling. Recrystallisation gave the product as

white crystals (1.0 g, 50%), m. p.  $78^{\circ}$  (methanol),

$\nu_{\text{max.}}$  840 ( $\text{:CH}$ )  $\text{cm}^{-1}$ ,  $\tau$  [ $\text{CDCl}_3$ ] 2.60-3.23 (m, 14H, ArH; 1H,  $\text{:CH}$ ),

Found: C, 82.31; H, 5.29%.

Calc. for  $\text{C}_{20}\text{H}_{15}\text{Cl}$ : C, 82.63; H, 5.16%.

#### 4. PALLADIUM (II) ASSISTED REACTIONS OF ALKENES

##### 4.1 REACTION CONDITIONS

Three sets of reaction conditions were used:

(1) The reaction mixture was stirred magnetically in a round-bottomed flask fitted with a condenser and was heated at about  $78^{\circ}$  in an oil-bath, the temperature being accurately recorded.

(2) As (1) except that three reactions were carried out simultaneously.

(3) The reaction mixture was stirred magnetically and was heated by immersion of the reaction vessel in a solvent which was boiling under reflux. Unless stated otherwise, the solvent was carbon tetrachloride (b.p.  $76.8^{\circ}$ ). Some reactions were also carried out under an atmosphere of nitrogen.

##### 4.2 PALLADIUM ACETATE ASSISTED PHENYLATION OF STYRENE

A series of palladium acetate assisted phenylations of styrene was carried out under standard conditions. Styrene was chosen as the alkene because of its known high reactivity in this reaction<sup>15,48</sup> and also because analysis of the reaction mixture was easily performed by g.l.c. Benzene and acetic acid were purified as described previously [p. 26] and styrene was purified by distillation under reduced pressure.

The reaction procedure was as follows: styrene (1 molar equiv.), benzene (100 molar equiv.), acetic acid (50 molar equiv.) and palladium acetate, batch 2A, (1 molar equiv.), were mixed in the reaction vessel and the reaction carried out for 8 h under reaction conditions (1). The balance used to weigh those reactants was reproducible to within 0.2 mg and the smallest weight subject to this error was 52.1 mg (styrene) which gives an error of about 0.4%. This is, therefore, the greatest possible error in any reactant.

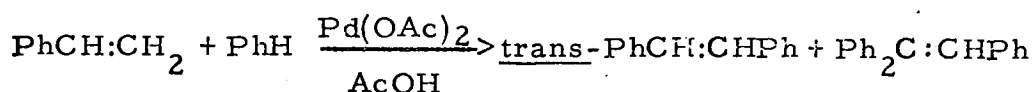
After reaction, the mixture was poured into sufficient 2N potassium hydroxide to neutralise all the acetic acid present

reaction of palladium is obtained, therefore, by addition of the percentage yield of stilbene remaining to twice that of triphenyl-ethylene.

#### 4.3 COMPARISON OF THE EFFECT OF PALLADIUM ACETATE BATCHES ON THE PHENYLATION OF STYRENE

A comparison of the effect of different batches of palladium acetate on the phenylation of styrene was carried out under reaction conditions (1) and (2). The internal standard for g.l.c. analysis (2.5% NPGS, 2m, ca. 200<sup>0</sup>) was either a non-reacting material (n-eicosane or n-docosane) added before reaction, or 4-methyl-trans-stilbene added after reaction but prior to analysis. The results are listed in Table 8.

Table 8      Product Distribution Obtained from the Palladium Acetate Assisted Phenylation of Styrene.      Various Batches of Palladium Acetate



$\text{Pd(OAc)}_2$ Batch	Stilbene (%)	TPE (%)	Total Stilbene (%)	Total Reaction of Palladium (%)
1	8.0	55.0	63.0	118.0
1	25.6	38.8	64.4	103.2
2A	51.1	3.5	54.6	58.1
2A	52.7	9.5	62.2	71.7
4E	11.5	64.5	76.0	140.5
9B	12.1	52.8	64.9	117.7
9B	36.0	37.0	73.0	110.0
9B	6.2	60.5	66.7	127.2
9B	3.7	65.0	68.7	133.7
10	25.4	45.8	71.2	117.0



Table 8 (cont)

Pd(OAc) <sub>2</sub> Batch	Stilbene (%)	TPE (%)	Total Stilbene (%)	Total Reaction of Palladium (%)
10	53.7	21.3	75.0	96.3
11	25.7	42.0	67.7	109.7
11	21.7	46.7	68.4	115.1
11	19.2	49.4	68.6	118.0
11	21.0	44.8	65.8	110.6

TPE:- triphenylethylene

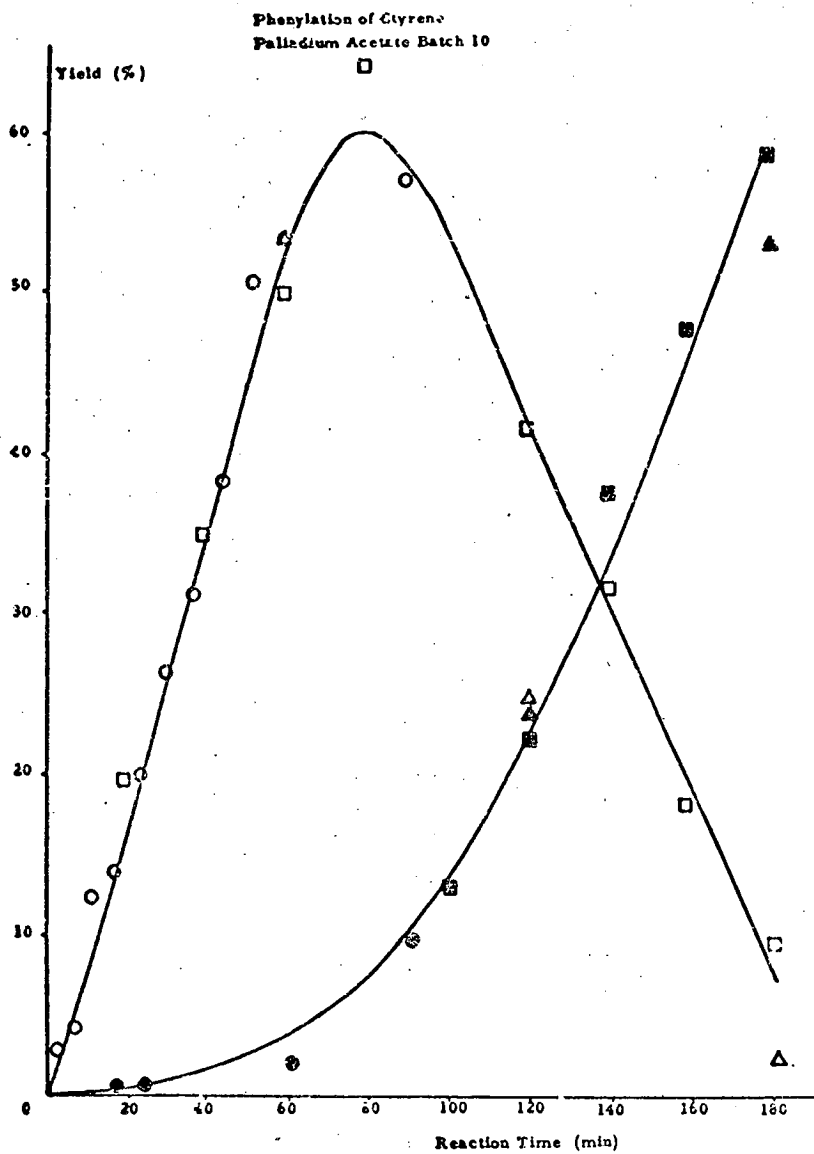
#### 4.4 KINETIC STUDY OF THE PALLADIUM ACETATE ASSISTED ARYLATION OF STYRENE

A kinetic study of the arylation of styrene was undertaken to determine at which stage of the reaction did formation of diarylated product become important. The composition of the reaction mixtures is shown in Table 9.

Table 9      Composition of Reaction Mixtures for Kinetic Studies

Palladium acetate	0.5 mmol (112.2mg)
Styrene	0.5 mmol (52.1 mg)
Benzene or Substituted benzene	} 50 mmol
Acetic acid	
	25 mmol (1.50 g)

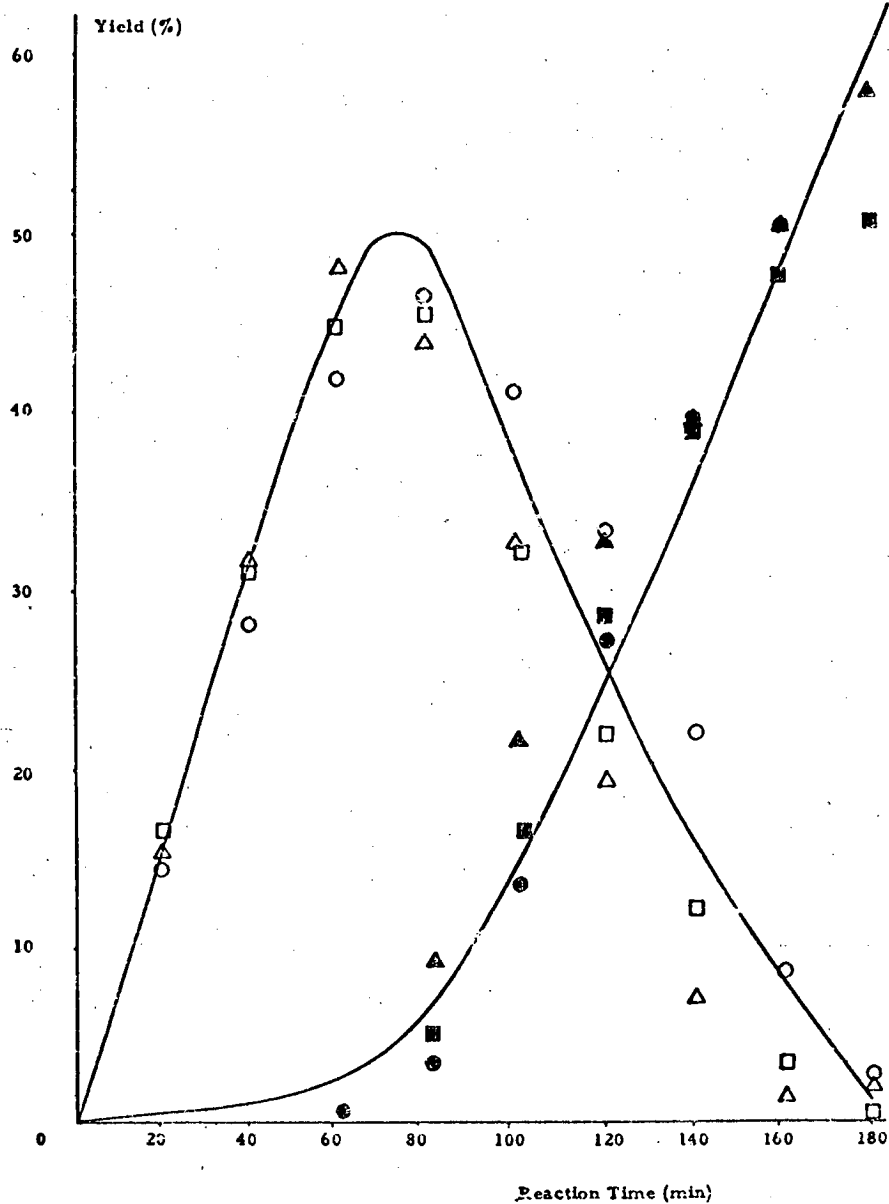
The reactions were carried out under conditions (3) and samples (ca. 0.025 ml) were removed at intervals using a 1 ml calibrated syringe. Each sample was placed in a small stoppered tube containing 2N potassium hydroxide (ca. 0.5 ml) and ether (ca. 0.5 ml) and stored at -20° until analysed by g.l.c. The reaction mixture contained an inert internal standard (n-docosane) against



1	2	3	
○	□	△	<u>trans</u> -stilbene
●	■	▲	triphenylethylene

Figure 2A

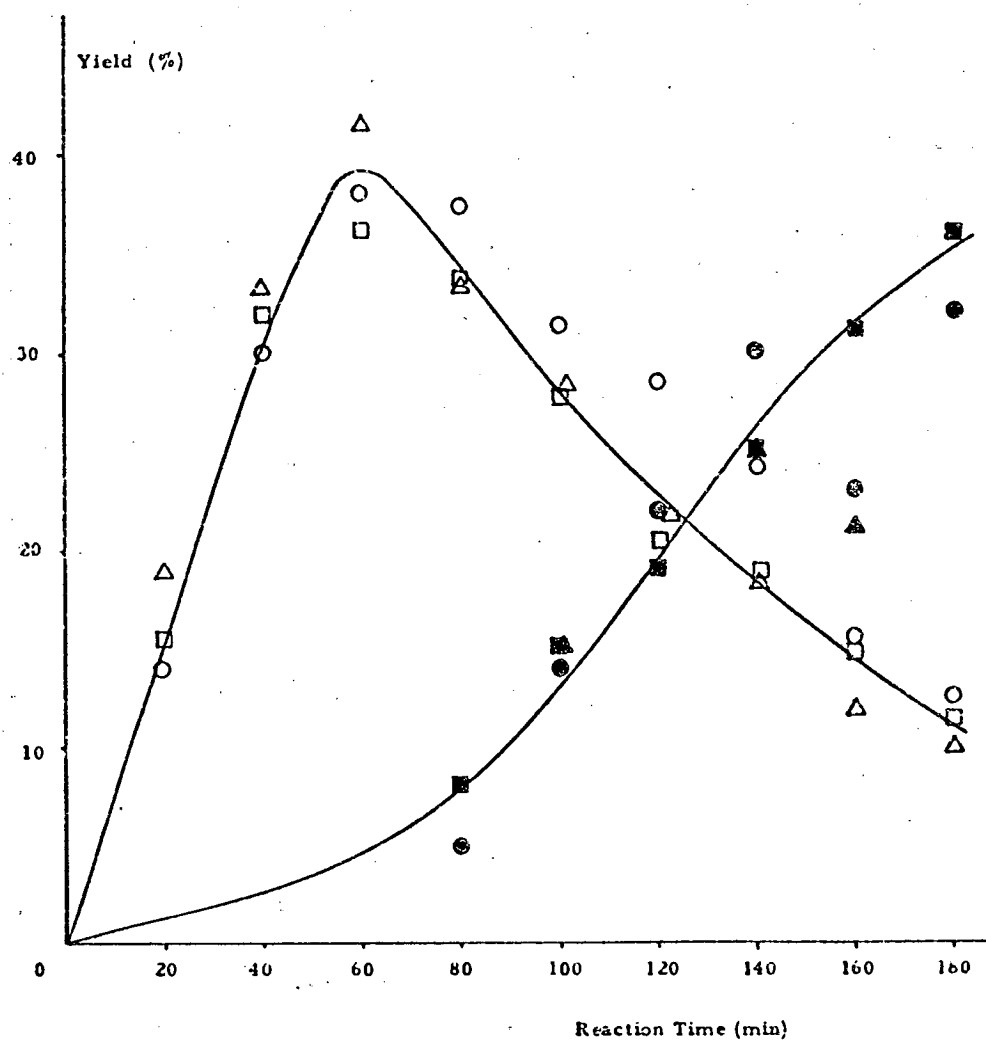
Phenylation of Styrene  
Palladium Acetate Batch 11



1	2	3	
○	□	△	<u>trans-stilbene</u>
●	■	▲	triphenylethylene

Figure 2B

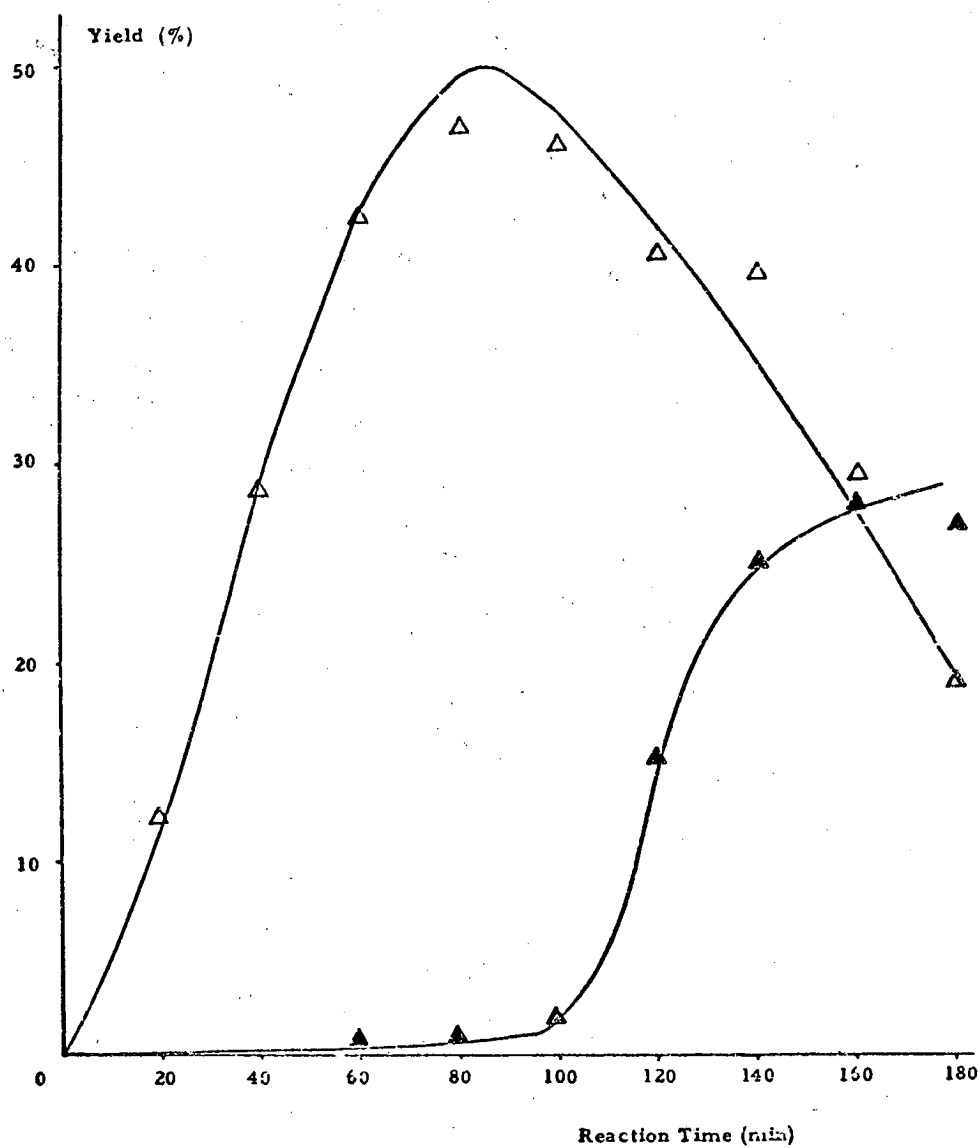
Arylation of Styrene with p-Xylene  
Palladium Acetate Batch 10



1	2	3	
○	□	△	2, 5-dimethyl- <u>trans</u> -stilbene
●	■	▲	diarylated product

Figure 3A

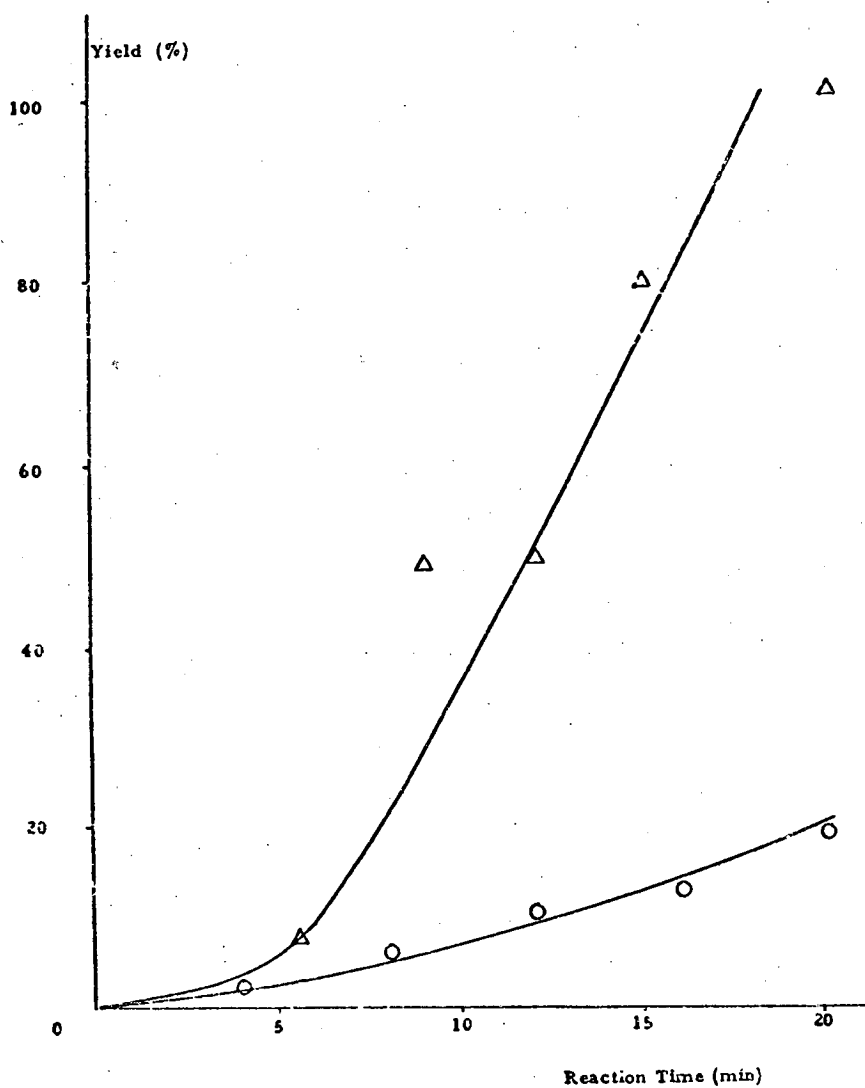
Arylation of Styrene with p-Xylene  
Palladium Acetate Batch 11



△ 2,5-dimethyl-trans-stilbene  
▲ diarylated product

Figure 3B

Arylation of Styrene with Anisole and Toluene  
Palladium Acetate Batch 11



Δ methoxy-trans-stilbene  
○ methyl-trans-stilbene

Figure 4

which the appearance of both the stilbene and triphenylethylene were measured. Two batches of palladium acetate (10 and 11) were used.

The phenylation of styrene was carried out three times with each batch of palladium acetate and the appearance and disappearance of the products are shown in Figure 2. A similar study of the arylation of styrene with *p*-xylene was carried out and the results are shown in Figure 3. Kinetic studies of the arylation of styrene with anisole and with toluene were each performed once and the appearance of each arylated product is shown in Figure 4.

#### 4.5 COMPETITIVE ARYLATIONS OF STYRENE ASSISTED BY PALLADIUM ACETATE

A series of reactions in which styrene was allowed to react with a large excess of an equimolar mixture of benzene and substituted benzene was carried out under reaction conditions (3) for 20 to 45 min. The composition of the reaction mixtures is given in Table 10.

Table 10      Composition of Reaction Mixtures for Competitive Arylations of Styrene

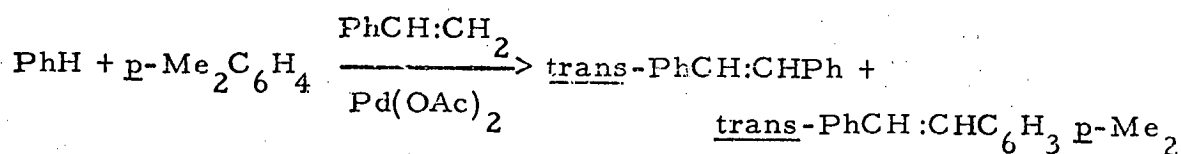
Palladium acetate	0.5 mmol (112.2 mg)
Styrene	0.5 mmol (52.1 mg)
Benzene	25 mmol (1.95 g)
Substituted benzene	25 mmol
Acetic acid	25 mmol (1.50 g)

The reaction mixtures were worked up as described [p. 36]. The isomer distribution of substituted stilbene and the absolute yields of stilbene and substituted stilbenes were determined by g.l.c. using *n*-docosane as internal standard. Substituted stilbenes were identified by comparison of retention times with authentic material or by analysis by mass spectrometry.

The competitive arylation with benzene and *p*-xylene was the

most easily analysed because only two monoarylation products, trans-stilbene and 2,5-dimethyl-trans-stilbene, are possible. This competitive reaction was carried out for either 30 min or 45 min with different batches of palladium acetate and the partial rate factor for p-xylene and the reactivity ratio,  $k_X/k_H$ , which is derived from the ratio of substituted stilbene to stilbene were calculated and are shown in Table 11.

Table 11      Competitive Arylation of Styrene with Benzene and  
p-Xylene with Various Batches of Palladium Acetate



$\text{Pd(OAc)}_2$ Batch	Stilbene (%)	Substituted Stilbene (%)	Partial Rate Factor	Reactivity Ratio ( $k_X/k_H$ )
6B	5.95	8.98	2.26	1.51
6B	6.83	8.82	1.94	1.29
11	7.96	11.04	2.09	1.39
11	9.15	13.10	2.15	1.43
11	8.52	11.95	2.10	1.40*
14A	9.94	11.61	1.75	1.17
14A	8.00	11.79	2.21	1.47
14B	8.17	11.79	2.16	1.44
14B	8.33	12.31	2.22	1.48
9B	15.40	22.42	2.18	1.46 <sup>†</sup>
9B	11.39	16.53	2.18	1.45 <sup>†</sup>
10	12.42	15.16	1.83	1.22 <sup>†</sup>
10	11.98	14.92	1.87	1.25 <sup>†</sup>
11	12.73	15.72	1.85	1.23 <sup>†</sup>
11	18.19	22.55	1.86	1.24 <sup>†</sup>

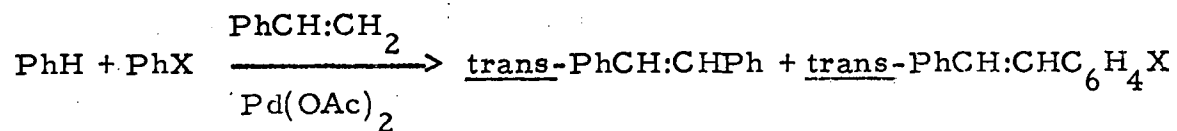
\* Reaction carried out under an atmosphere of nitrogen.

<sup>†</sup> Reaction time 45 min. All other reaction times 30 min.



Table 12

## Competitive Arylation of Styrene



X	Pd(OAc) <sub>2</sub> Batch	Product o	Isomer m	Distribution (%) p	Stilbene (%)	Substituted Stilbene (%)	Partial f <sub>o</sub>	Rate f <sub>m</sub>	Factors f <sub>p</sub>	Reactivity Ratio (k <sub>X</sub> /k <sub>H</sub> )
Me	10	27.63		72.63*	15.29	23.20	1.26	≤3.31	≤6.62	1.52 <sup>†</sup>
Me	11	27.54		72.46*	15.12	22.66	1.24	≤3.26	≤6.52	1.50 <sup>†</sup>
OMe	10	32.99	5.24	61.77	6.85	40.07	5.79	0.92	21.68	5.85 <sup>†</sup>
OMe	11	33.02	5.04	61.93	6.98	39.51	5.61	0.86	21.03	5.66 <sup>†</sup>
CF <sub>3</sub>	10	← 100 →			13.77	1.97	≤0.42	≤0.42	≤0.84	0.14
CF <sub>3</sub>	11	← 100 →			14.22	1.98	≤0.42	≤0.42	≤0.84	0.14
Cl	10	31.10		68.90*	21.40	13.60	0.59	≤1.32	≤2.65	0.64
Cl	11	30.36		69.63*	13.77	8.30	0.55	≤1.25	≤2.51	0.60

\* Total meta- plus para-isomers

<sup>†</sup> Reaction time 20 min. All other reactions 30 min.

Similar information was determined from competitive arylations with benzene and other aromatic compounds and is listed in Table 12.

Because not all isomers of the substituted stilbenes could be separated by g.l.c., partial rate factors quoted for toluene, trifluoromethylbenzene and chlorobenzene are the maximum possible values. For example, for trifluoromethylbenzene the maximum partial rate factor for the ortho-position,  $f_o$ , is calculated assuming that  $f_m = f_p = 0$  and similarly for the other positions.

#### 4.6 COMPETITIVE ALKENYLATIONS OF BENZENE ASSISTED BY PALLADIUM ACETATE

A series of reactions was performed in which benzene was allowed to react with an equimolar mixture of styrene and a ring-substituted styrene under reaction conditions (3). The composition of the reaction mixtures is shown in Table 13.

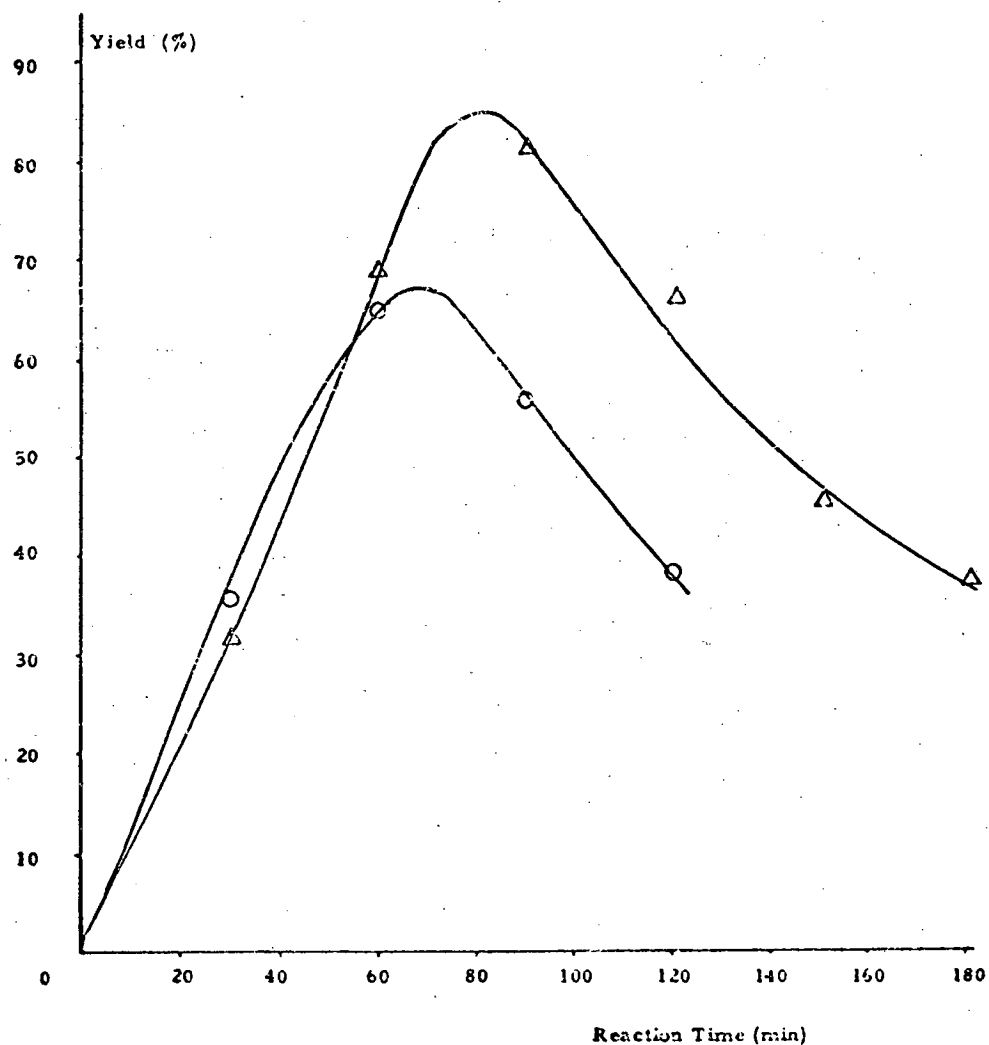
Table 13      Composition of Reaction Mixtures in the Competitive Alkenylation of Benzene

Palladium acetate	0.5 mmol (112.2 mg)
Styrene	0.25 mmol (26.1 mg)
Substituted styrene	0.25 mmol
Benzene	50 mmol (3.90 g)
Acetic acid	25 mmol (1.50 g)

The reaction mixtures were worked up as described previously [p. 36] and the absolute yields of trans-stilbene and substituted stilbene were determined by g.l.c. analysis using n-docosane as internal standard. Because both styrenes are minor components of the reaction mixture it is important that the reaction be studied over only the first few per cent of reaction so that the concentration of each styrene remains as constant as possible.

A kinetic study of the phenylation of 4-methylstyrene was

Phenylation of 4-Methylstyrene



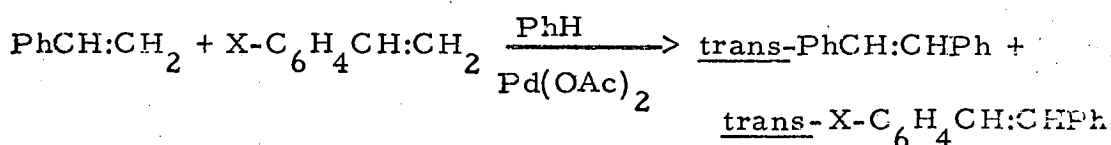
- Δ 4-methyl-trans-stilbene:palladium acetate batch 10  
○ 4-methyl-trans-stilbene:palladium acetate batch 11

Figure 5

carried out with palladium acetate (batches 10 and 11) to give an indication of the reaction rate. The composition of the reaction mixture and the reaction conditions were as described in Experimental Section 4.4, p.39 and analysis of the product mixture was by g.l.c. with n-docosane as internal standard. The variation in yield of 4-methyl-trans-stilbene with time is illustrated in Figure 5.

So that only a few per cent of each styrene would undergo phenylation the competitive alkenylation of benzene was carried out for 8 min except in one case in which the reaction time was 20 min. Table 14 lists the yields of each stilbene and the reactivity ratio ( $k_X/k_H$ ).

Table 14      Competitive Alkenylation of Benzene



X	Pd(OAc) <sub>2</sub> Batch	Stilbene (%)	Substituted Stilbene (%)	Reactivity Ratio ( $k_X/k_H$ )
4-Me	10	7.17	6.97	0.97*
4-Me	11	7.32	8.01	1.09*
4-Me	10	2.10	1.85	0.88
4-Me	11	2.12	2.05	0.97
4-Cl	10	2.63	1.96	0.75
3-CF <sub>3</sub>	10	2.90	3.07	1.06
3-CF <sub>3</sub>	11	2.84	2.90	1.02

\* Reaction time:- 20 min.

It should be noted that a similar competitive alkenylation of benzene with styrene and 3,3-dimethylbut-1-ene was carried out

under identical conditions for 8 min with palladium acetate, batch 11. The yields of trans-stilbene and 3, 3-dimethyl-1-phenylbut-1-ene obtained were 9.30% and 2.26% respectively which gives a reactivity ratio ( $k_X/k_H$ ) of 0.24.

#### 4.7 THE EFFECT OF REACTANT RATIO ON THE PHENYLATION OF STYRENE

A series of styrene phenylations with palladium acetate, batch 2A, in which the amount of styrene relative to benzene and palladium acetate was varied, was performed under reaction conditions (1) for 8 h. The work-up was described previously [ p. 36]. Each product mixture was analysed by g.l.c. for trans-stilbene, triphenylethylene and the styrene coupling product, 1,4-diphenylbuta-1,3-diene, the internal standard being 4-methyl-trans-stilbene which was added to the product mixture after reaction. Products were identified by comparison of g.l.c. retention times and by mass-spectrometric analysis and the yields of each product are shown in Table 15.

Table 15      Effect of Reactant Ratio on Product Distribution.  
Palladium Acetate Batch 2A

Reactants (molar equiv.)			Products (%)			Reaction of Palladium (%)
B	S	P	t-stb	TPE	DPB	
100	1	1*	32.3	20.4	0	73.1
100	1	1	39.7	14.3	0	68.3
100	1	1	2.0	40.0	0	82.0
100	5	1	19.1	3±1	7±1	32±3
100	10	1	21.2	5±1	23±1	54±3
100	20	1	8.5	0	10±1	19±1

\* The standard quantity of palladium acetate used was 0.5 mmol (112.2 mg)

B:- benzene; S:- styrene; P:- palladium acetate;

t-stb:- trans-stilbene; TPE:- triphenylethylene;

DPB:- 1,4-diphenylbuta-1,3-diene.

The yield of triphenylethylene, the product derived from phenylation of stilbene is, in some cases, approximate because the alkene coupled product, which was incompletely separated from triphenylethylene by g.l.c., was found to be present in varying amounts.

A similar series of styrene phenylations with palladium acetate, batch 3A, in which the amounts of styrene and palladium acetate were varied with respect to benzene, was carried out under identical conditions to those described above. Table 16 lists the yields of each product found by g.l.c. analysis.

Table 16      Effect of Reactant Ratio on Product Distribution.  
Palladium Acetate Batch 3A

Reactants (molar equiv)			Products (%)			Reaction of Palladium (%)
B	S	P	t-stb	TPE	DPB	
100	1	1*	51.1	3.5	0	58.1
100	1	1	52.7	9.5	0	71.7
100	1.25	1.25	37.9	12 $\pm$ 1	1 $\pm$ 1	63 $\pm$ 3
100	1.25	1.25	35.4	17 $\pm$ 1	1 $\pm$ 1	70 $\pm$ 3
100	1.66	1.66	23.8	16 $\pm$ 1	1 $\pm$ 1	57 $\pm$ 3
100	1.66	1.66	48.4	6 $\pm$ 1	1 $\pm$ 1	61 $\pm$ 3
100	2.5	2.5	30.8	6 $\pm$ 1	1 $\pm$ 1	44 $\pm$ 3

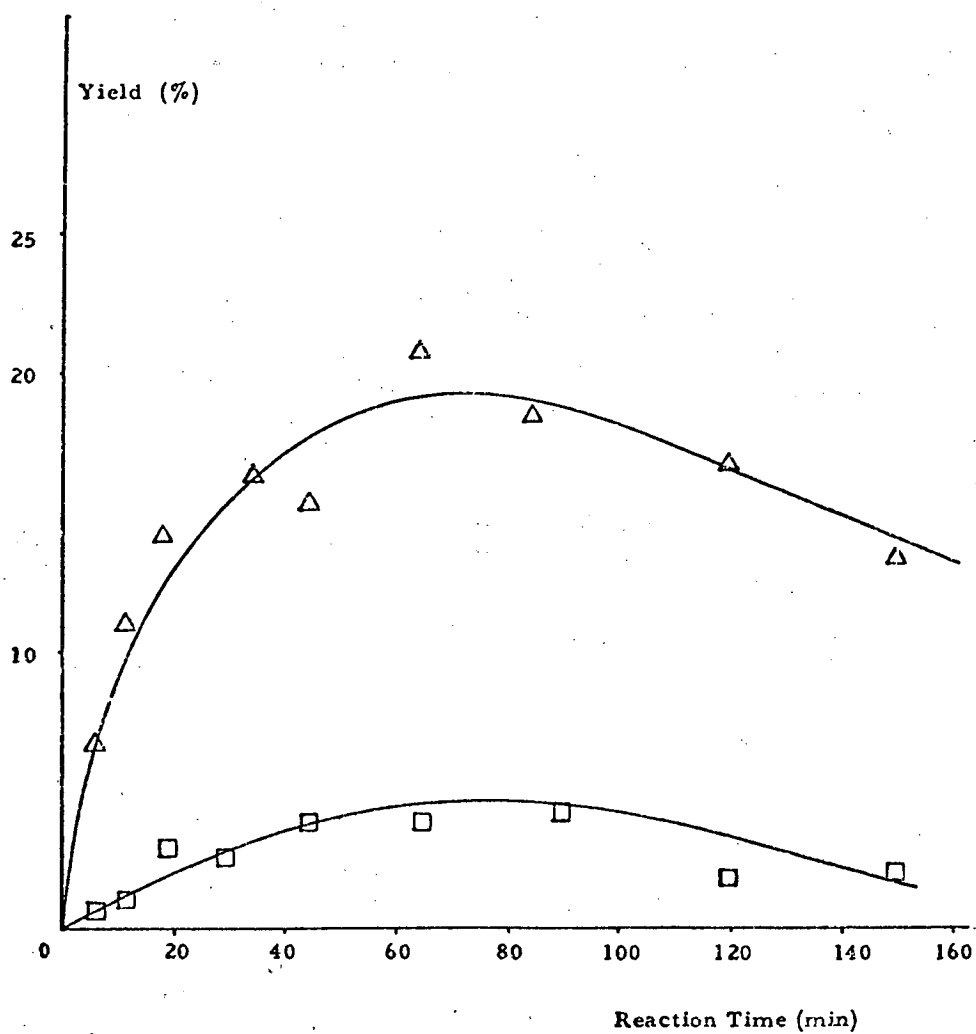
\* The standard quantity of palladium acetate used was 0.5 mmol (112.2 mg).

B:- benzene; S:- styrene; P:- palladium acetate;

t-stb:- trans-stilbene; TPE:- triphenylethylene;

DPB:- 1,4-diphenylbuta-1,3-diene.

**Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene**

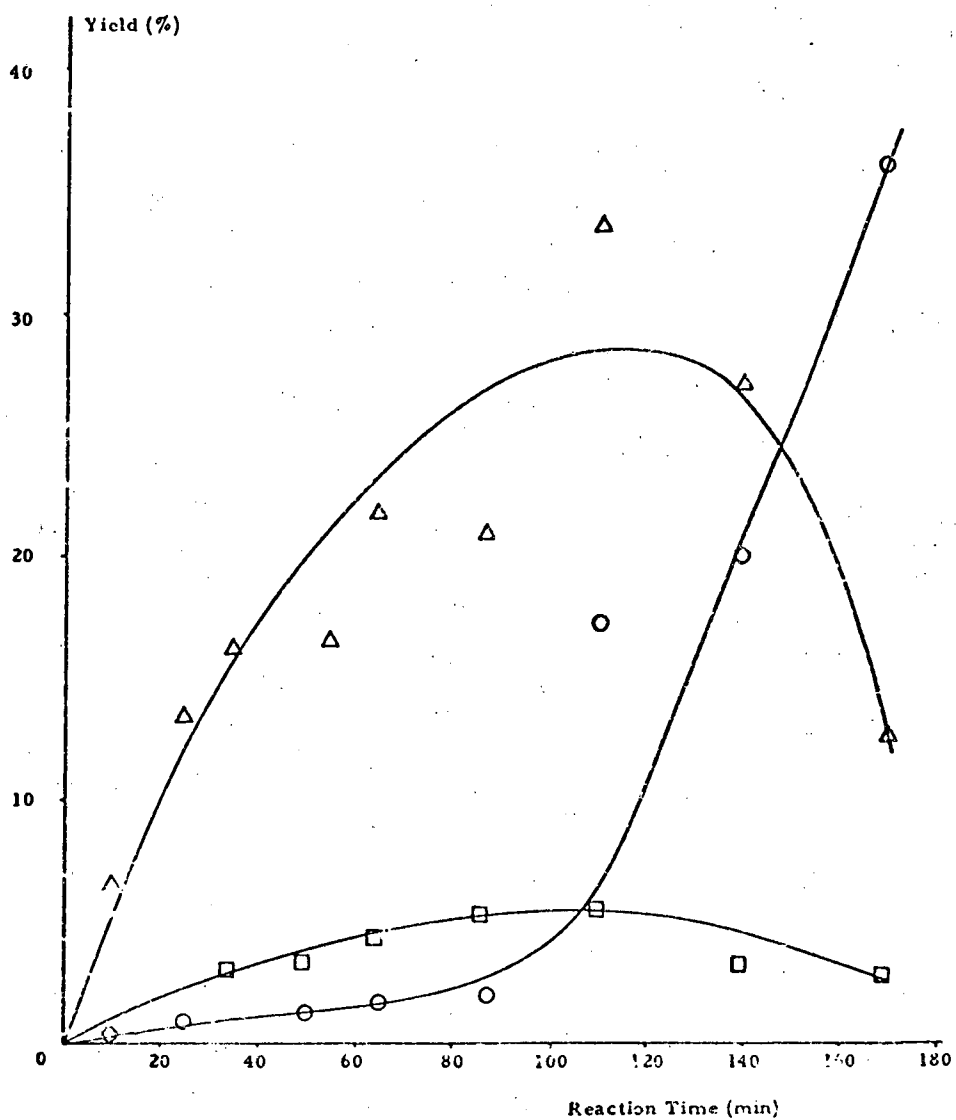


PhH:styrene:Pd(OAc)<sub>2</sub>  
200 : 1 : 1

- △ trans-stilbene  
□ 1,4-diphenylbuta-1,3-diene

**Figure 6a**

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene



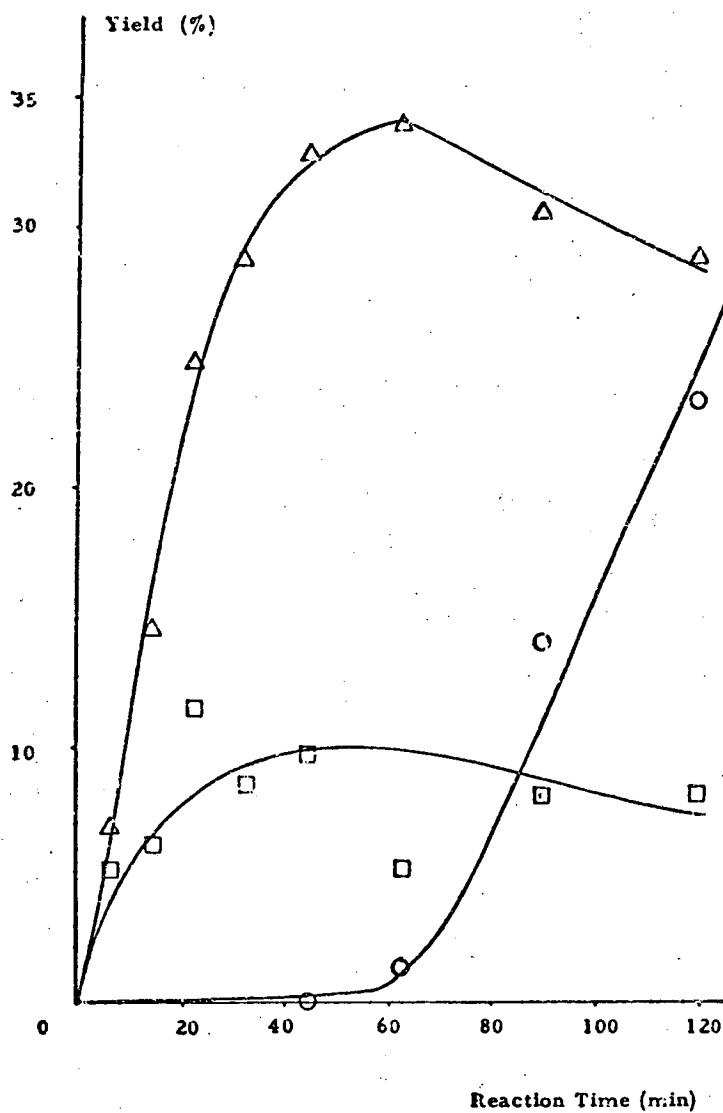
PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 1 : 1

- △ trans-stilbene
- triphenylethylene
- 1,4-diphenylbuta-1,3-diene

Figure 6b



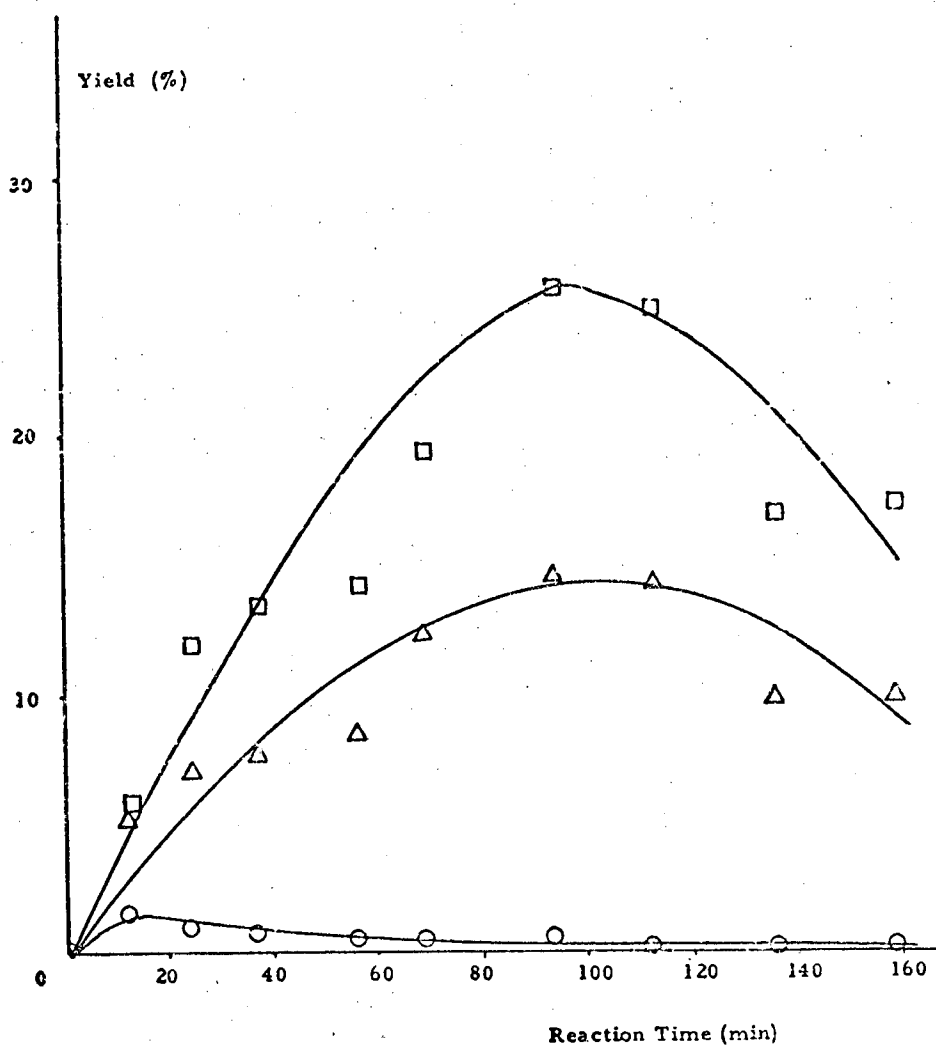
Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene



- Δ trans-stilbene  
 ○ triphenylethylene  
 □ 1,4-diphenylbuta-1,3-diene

Figure 6c

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene

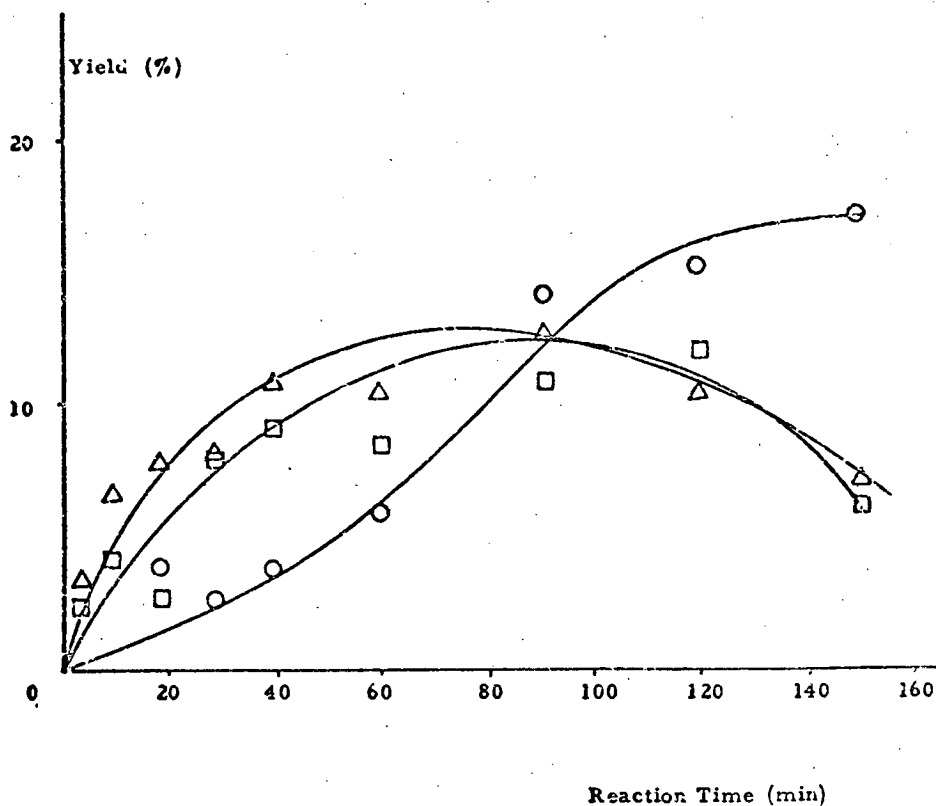


PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 5 : 1

- △ trans-stilbene
- triphenylethylene
- 1,4-diphenylbuta-1,3-diene

Figure 6d

Effect of Reactant Ratio on Product Distribution  
In the Phenylation of Styrene

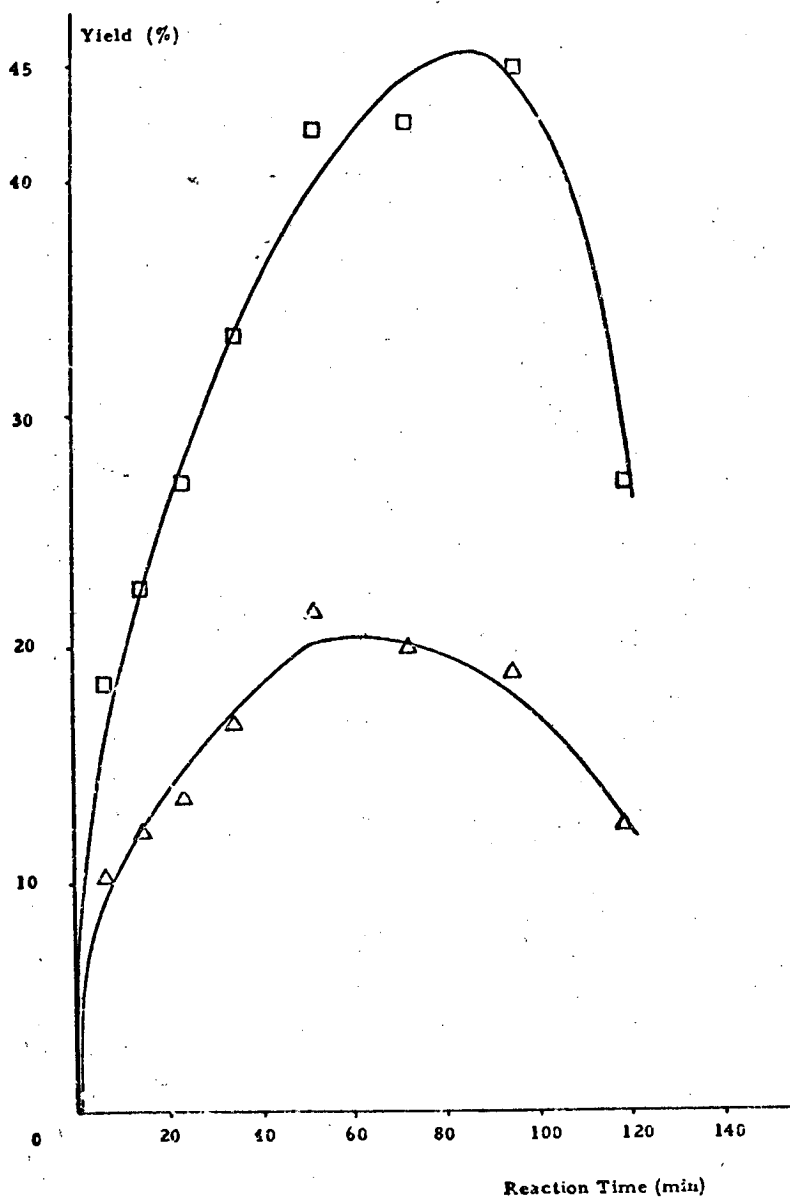


PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 5 : 5

- $\Delta$  trans-stilbene  
 $\square$  1,4-diphenylbuta-1,3-diene

Figure 6e

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene

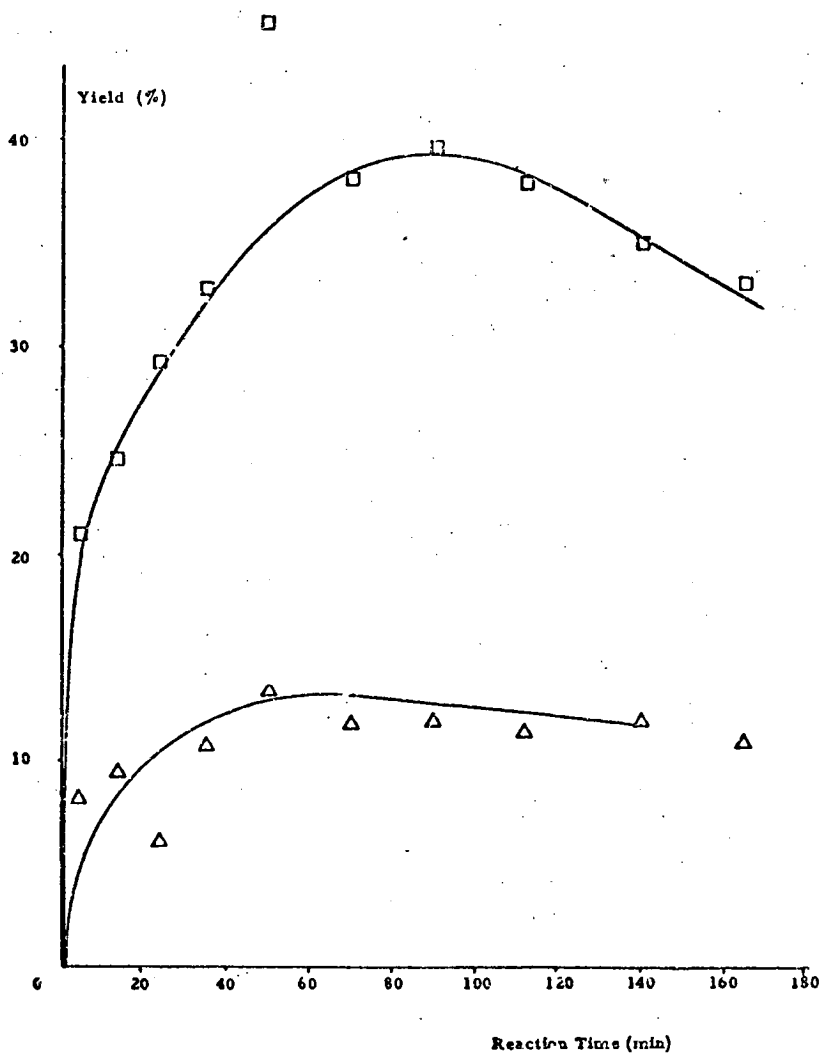


PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 10 : 1

- Δ trans-stilbene  
□ 1,4-diphenylbuta-1,3-diene

Figure 6f

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene



PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 20 : 1

- Δ trans-stilbene  
□ 1,4-diphenylbuta-1,3-diene

Figure 6g

A kinetic study of the effect of altering the reactant ratio was carried out using palladium acetate, batch 11, under reaction conditions (3) under an atmosphere of nitrogen, the same analytical method being employed as that used in the previous studies of the effect of reactant ratio on product distribution. The composition of the reaction mixtures is shown in Table 17.

Table 17      Composition of Reaction Mixtures in the Kinetic Study of the Effect of Reactant Ratio on the Phenylation of Styrene (mmol)

Reaction number	1	2	3	4	5	6	7
Palladium acetate	0.25	0.5	1	0.5	2.5	0.5	0.5
Styrene	0.25	0.5	1	2.5	2.5	5	10
Benzene	50	50	50	50	50	50	50
Acetic acid	25	25	25	25	25	25	25

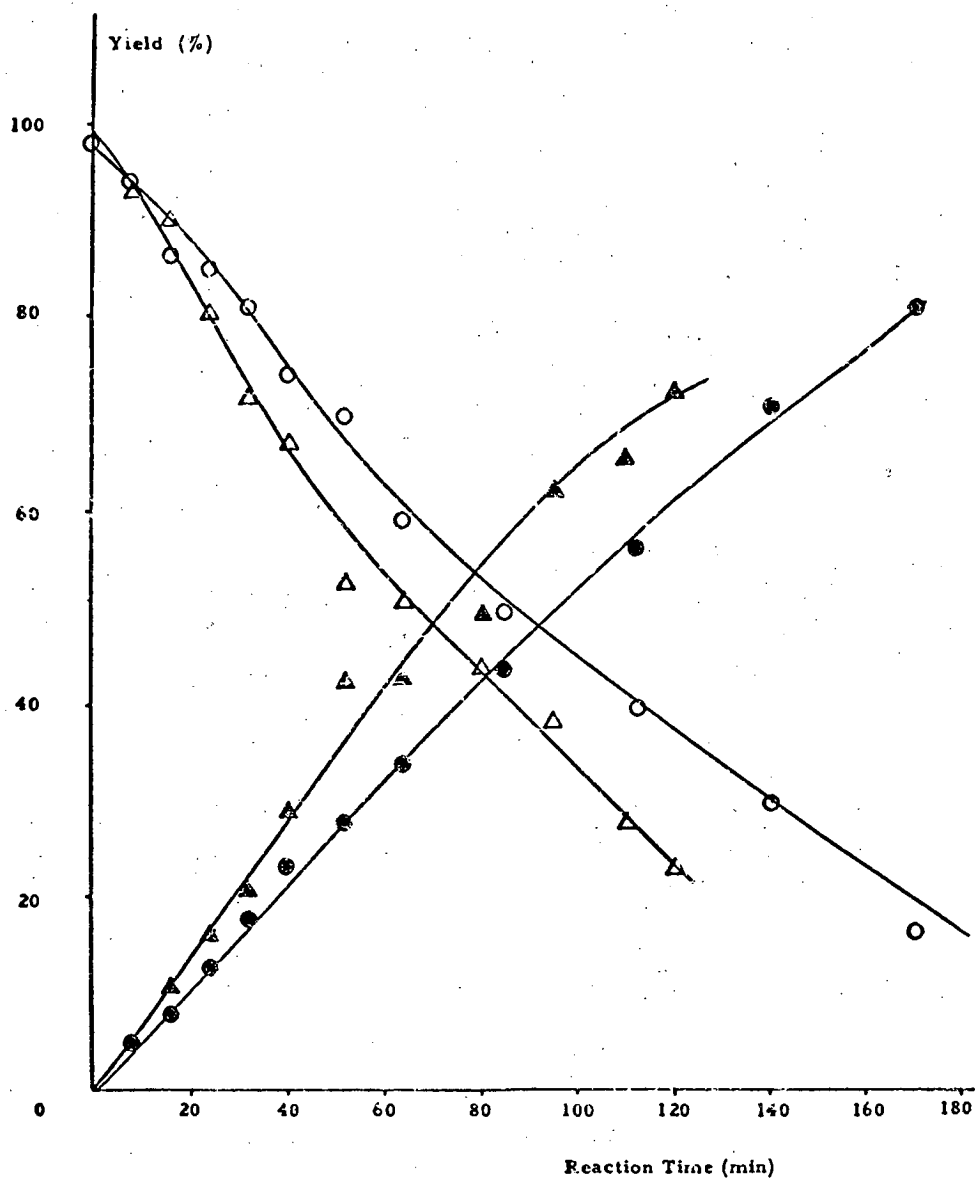
The appearance and disappearance of the products, trans-stilbene, triphenylethylene and 1,4-diphenylbuta-1,3-diene, were followed by g.l.c. with n-docosane as internal standard and these results are represented in Figure 6.

#### 4.8      PHENYLATION OF ALKENES OTHER THAN STYRENES

##### 4.8(a) trans-Stilbene

The phenylation of trans-stilbene assisted by palladium acetate was carried out under reaction conditions (3) for different times to determine the total conversion of stilbene to triphenylethylene. The composition of the reaction mixtures is shown in Table 18 and the yields of triphenylethylene determined by g.l.c. are listed in Table 19.

# Phenylation of trans-Stilbene



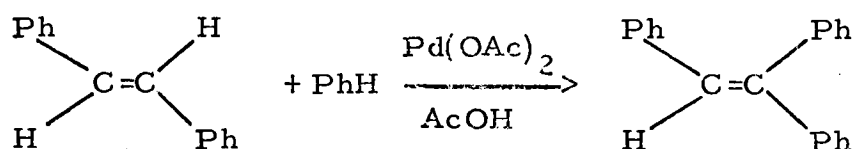
- trans-stilbene
  - triphenylethylene
  - △ trans-stilbene
  - ▲ triphenylethylene
- } under atmosphere of nitrogen

Figure 7

Table 18      Composition of Reaction Mixtures in the  
Phenylation of trans-Stilbene

Palladium acetate	0.5 mmol (112.2 mg)
<u>trans</u> -Stilbene	0.5 mmol (90.1 mg)
Benzene	50 mmol (3.90 g)
Acetic acid	25 mmol (1.50 g)

Table 19      Triphenylethylene Yield in the Phenylation of  
trans-Stilbene Assisted by Palladium Acetate



$\text{Pd(OAc)}_2$ Batch	Reaction Time (h)	TPE (%)
10	3.0	94.3
11	3.6	97.8
11	20.0	78.0

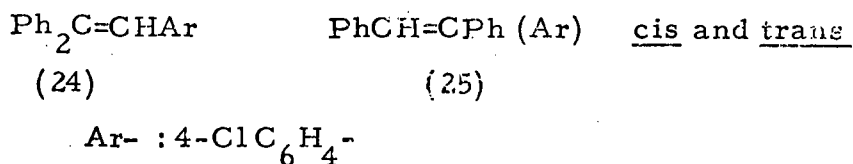
TPE:- triphenylethylene

A kinetic study of the phenylation of trans-stilbene was carried out in which trans-stilbene was allowed to react with an excess of benzene under reaction conditions (3) both open to the atmosphere and under an atmosphere of nitrogen. The composition of the reaction mixtures was the same as shown in Table 18 and the same method as used in previous kinetic studies was employed, product analysis being by g.l.c. with n-docosane as internal standard. The disappearance of trans-stilbene and the appearance of triphenylethylene with time are illustrated in Figure 7.



#### 4.8(b) 4-Chloro-trans-stilbene

The phenylation of 4-chloro-trans-stilbene assisted by palladium acetate was carried out once under reaction conditions (3) for 1 h, the reaction mixture having a composition identical to that shown in Table 18. Complete separation by g.l.c. of the phenylated products, 2-(4-chlorophenyl)-1,1-diphenylethylene (24) and 1-(4-chlorophenyl)-1,2-diphenylethylene [cis and trans] (25) was not possible and so determination of the relative amounts of each product was performed by comparing the ratio of the peak heights of the two products with the ratio of peak heights of different mixtures of authentic samples until the two ratios were almost identical.



The ratio of products (24)/(25) was found to be ca. 1.2.

#### 4.8(c) Indene

The phenylation of indene assisted by palladium acetate was carried out by the same method and under the same conditions (1), for 8 h as described in Experimental Section 4.2 [p. 36] for the phenylation of styrene, the normal work-up affording a red ethereal solution (a yellow ethereal solution is obtained from styrene phenylation). The product mixture was analysed qualitatively by g.l.c. and by g.l.c./m.s., four products and indene itself being identified; three phenylated indenenes and an acetoxylated indene. The three phenylated indenenes were assigned by analysis of their mass spectra, two of the three having the same fragmentation pattern. Measurement of peak areas (peak height x width at half peak height) suggests that the proportion of each compound in the product mixture is as shown in Table 20.

Table 20      Proportion of Products in the Phenylation of Indene

Indene	1
Acetoxylated indene	1
1-Phenylindene	1
2-Phenylindene	4
3-Phenylindene	1

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4.9      OTHER REACTIONS RELATED TO STYRENE  
PHENYLATION

4.9(a) Palladium Acetate Assisted Biphenyl Formation (Absence of Styrene)

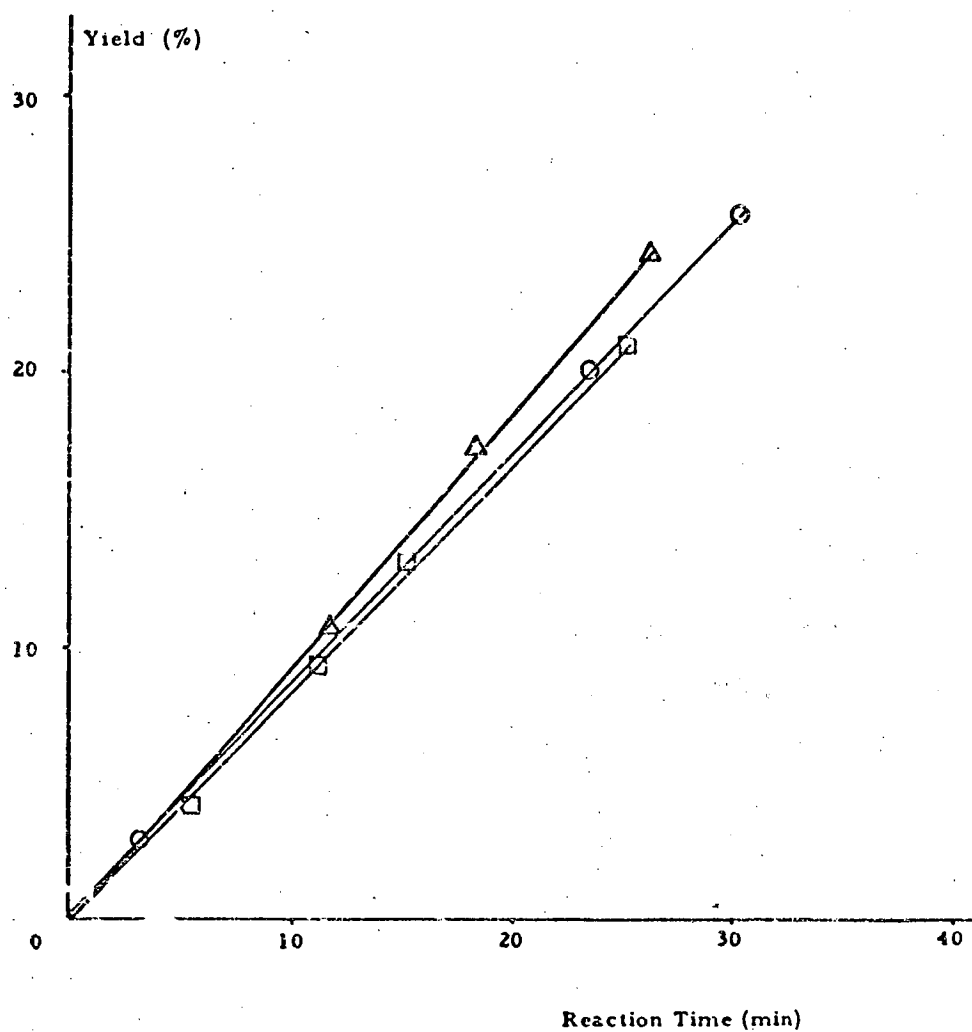
A kinetic study of the palladium acetate (batch 12) assisted coupling reaction of benzene was carried out under reaction conditions (3) over a period of 3 h using the same method as employed in previous kinetic studies. The composition of the reaction mixture is shown in Table 21.

Table 21      Reaction Mixture Composition in Palladium Acetate Assisted Biphenyl Formation

Palladium acetate	0.5 mmol (112.2 mg)
Benzene	50 mmol (3.90 g)
Acetic acid	25 mmol (1.50 g)

---

Analysis of the reaction mixture was by g.l.c., the internal standard being n-docosane. The results calculated are shown in Table 22.

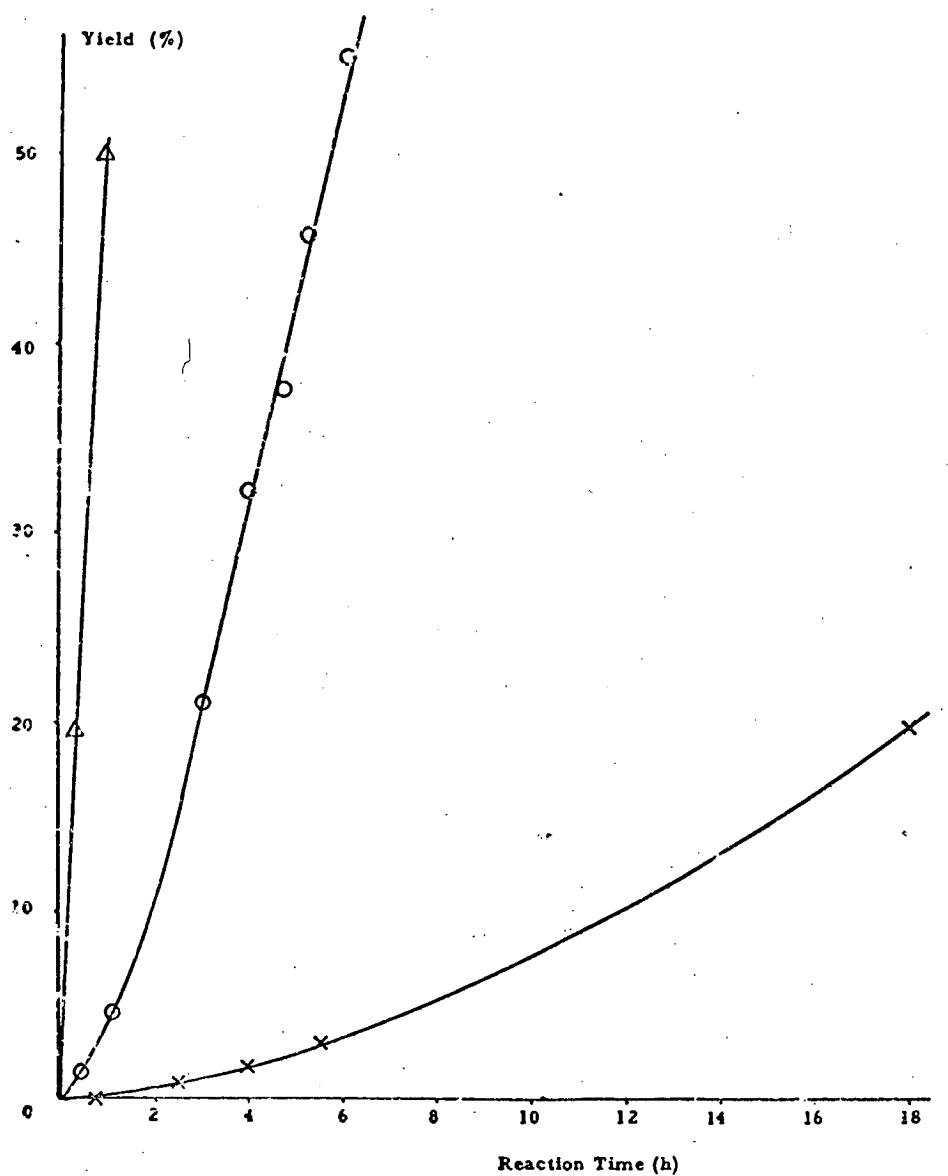


stilbene

- 'normal' phenylation of styrene
- △ Run 1 styrene addition to reaction
- Run 2 mixture 4.9(a)

Figure 8

Effect of Temperature on Styrene Phenylation



X     39-41°  
O     61-62°  
Δ     77°

Figure 9

Table 22    Yields of Biphenyl in Palladium Acetate Assisted  
Coupling of Benzene

Reaction Time (h)	Biphenyl (%)
0.5	1.0
1.0	1.9
1.5	4.2
3.0	6.0

4.9(b)    Effect of Addition of Styrene to Reaction Mixture 4.9(a)

A reaction identical to that described above was carried out with the exception that styrene was added to the biphenyl reaction mixture after 75 min and the reaction mixture then analysed at intervals by g.l.c. for trans-stilbene. The yield of biphenyl after 75 min reaction was 2.7 per cent, and the appearance of trans-stilbene is represented in Figure 8 which also shows the appearance of trans-stilbene in the 'normal' phenylation of styrene.

4.9(c)    Temperature Dependence of the Palladium Acetate  
Assisted Phenylation of Styrene

A kinetic study of the effect of temperature change on the palladium acetate (batch 11) assisted phenylation of styrene was performed under reaction conditions (3) at three temperatures; 39-41° (b.p. methylene chloride), 61-62° (b.p. chloroform) and 77° (b.p. carbon tetrachloride). Analysis of the product mixture was carried out by g.l.c. as in previous kinetic studies [Experimental Section 4.4, p. 39]. The composition of the reaction mixtures is the same as described in Table 9, p. 39 and Figure 9 illustrates the dependence of trans-stilbene formation on temperature.

#### 4.10 STYRENE PHENYLATION ASSISTED BY PALLADIUM (O) OR PALLADIUM (II) COMPOUNDS OTHER THAN PALLADIUM ACETATE

##### 4.10(a) Palladium Metal

It was found that reaction of bromobenzene with styrene in the presence of palladium sponge (prepared by reduction of palladium (II) chloride by hydrazine hydrate) under reaction conditions (1) for 8 h afforded trans-stilbene.

##### 4.10(b) Palladium Propionate

Phenylation of styrene assisted by palladium propionate was carried out under reaction conditions (2) for 8 h. The composition of the reaction mixtures was the same as described in Table 9, p. 39 and analysis of the reaction mixture was performed by g.l.c., the yields of trans-stilbene and triphenylethylene being shown in Table 23.

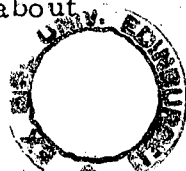
Table 23      Phenylation of Styrene with Palladium Propionate

<u>Stilbene (%)</u>	<u>TPE (%)</u>	<u>Reaction of Palladium (%)</u>
23.98	45.88	115.74
61.28	4.84	70.96

TPE:- triphenylethylene

##### 4.10(c) Palladium Benzoate

The styrene phenylation assisted by palladium benzoate was carried out in an identical manner to that used in the palladium propionate assisted styrene phenylation. Due to a fault in the integrator only qualitative g.l.c. analysis was performed, and no trans-stilbene was found, triphenylethylene being the major product. Very few products volatile by g.l.c. were found and so the yield of triphenylethylene is estimated at about 80%. A yield of this magnitude necessitates that the total reaction of the palladium complex be about 160%.



#### 4.10(d) Dichlorobis(benzonitrile)palladium (II)

Attempts were made to phenylate styrene in the presence of dichlorobis(benzonitrile)palladium (II) under reaction conditions (2) for 8 h. The composition of the reaction mixtures is shown in Table 24.

Table 24      Composition of Reaction Mixtures in Styrene  
Phenylation Assisted by Dichlorobis(benzonitrile)-  
palladium (II)

(PhCN) <sub>2</sub> PdCl <sub>2</sub>	0.5 mmol (196.7 mg)
Styrene	0.5 mmol (52.1 mg)
Benzene	50 mmol (3.90 g)
Acetic acid	25 mmol (1.50 g)

The work-up of the reaction mixture was identical to that described for palladium acetate assisted phenylation of styrene, [Experimental Section 4.2, p 36] and analysis was by g.l.c. with 4-methyl-trans-stilbene as internal standard. The yields of trans-stilbene and triphenylethylene are listed in Table 25.

Table 25      Phenylation of Styrene Assisted by Dichlorobis-  
(benzonitrile)palladium (II)

Stilbene (%)	TPE (%)	Reaction of Palladium (%)
14.2	0.9	16.0
12.5	0.3	13.1

TPE:- triphenylethylene.

#### 4.10(e) Palladium Chloride and Sodium Acetate

A series of styrene phenylations was carried out by reaction of styrene with benzene in the presence of palladium chloride and sodium acetate in acetic acid. Palladium chloride, sodium acetate

and acetic acid were heated at 75° for either 0 h or 15 h after which styrene and benzene were added to the reaction mixture and the phenylation carried out under reaction conditions (2) for 8 h. The reaction mixture composition is shown in Table 26.

Table 26      Composition of Reaction Mixtures in the Phenylation of Styrene with Palladium Chloride and Sodium Acetate

Palladium chloride	0.5 mmol (88.7 mg)
Sodium acetate	1 mmol (82.0 mg)
Styrene	0.5 mmol (52.1 mg)
Benzene	50 mmol (3.90 g)
Acetic acid	25 mmol (1.50 g)

Work-up of the reaction mixtures was carried out as described previously [Experimental Section 4.2, p. 36] and analysis was by g.l.c., the yields of trans-stilbene and triphenylethylene being listed in Table 27.

Table 27      Phenylation of Styrene Assisted by Palladium Chloride and Sodium Acetate

Stilbene (%)	TPE (%)	Reaction of Palladium (%)
9.78	1.35	12.48*
32.94	2.94	38.82
25.11	12.83	50.77
25.78	1.47	28.72

\* Equilibration time 0 h.    Equilibration time for other reactions 15 h.

TPE:- triphenylethylene



#### 4.11 ATTEMPTS TO STUDY STYRENE PHENYLATION BY SPECTROSCOPIC TECHNIQUES

##### 4.11(a) Nuclear Magnetic Resonance Spectroscopy

An attempt was made to study styrene phenylation by observing changes in the resonances of the olefinic protons at 100 MHz in the absence and presence of palladium acetate. No change in the resonances of the olefinic protons was observed.

##### 4.11(b) Ultra-Violet Spectroscopy

An attempt was made to observe any change in the styrene absorption ( $\epsilon_{\text{max.}}^{6900}$ ) at 255 m $\mu$  in acetic acid at 80° on the addition of palladium acetate. The concentration of both styrene and palladium acetate was  $2.2 \times 10^{-4} \text{ mol l}^{-1}$ . Addition of palladium acetate gave no shift in absorption from 275 m $\mu$  and a change in the molar absorptivity,  $\epsilon_{\text{max.}}$ , of only about 4%.

However, a qualitative study of styrene phenylation was made, the composition of the reaction mixture being shown in Table 28.

Table 28      Composition of Reaction Mixtures for Styrene Phenylation. U. V. Study

Palladium acetate	<u>ca.</u> 10 molar equiv.
Styrene	<u>ca.</u> 5 molar equiv.
Benzene	100 molar equiv.
Acetic acid	50 molar equiv.

The u-v spectrum of possible products, trans-stilbene, 1,4-diphenylbuta-1,3-diene and biphenyl, in a benzene-acetic acid mixture (2:1) was run [reference cell, benzene-acetic acid 2:1]. The u. v. spectrum of palladium acetate in benzene-acetic acid was run periodically over 1 h after which styrene was added to both cells and the u. v. spectrum of the reaction mixture was now run periodically

over 7 h. Only absorptions due to the products, trans-stilbene and 1,4-diphenylbuta-1,3-diene, were observed.

#### 4.12 ATTEMPTED CYCLISATIONS OF ALKENES

Attempts were made to cyclise various alkenes in the presence of a palladium complex. The alkenes used in this study were 1-phenylbut-2-ene (PB), allylbenzene (AB) and allylphenyl ether (APE) and the palladium complexes were palladium acetate, palladium propionate and dichlorobis(benzonitrile)palladium.

A solution of the alkene (0.5 mmol) and palladium complex (0.5 mmol) in glacial acetic acid (1150-fold excess) was maintained at 77° for either 2.5 h or 3 h and the work-up was carried out as described for styrene phenylation [Experimental Section 4.2, p. 36]. Analysis of the product mixtures was by g.l.c. (5% CAR20M, 177°) and by g.l.c./m.s. at 40eV. Only the peak area of each product was determined and so the amount of each product was evaluated relative to the smallest product in each mixture. The results of the attempted cyclisations are listed in Table 29.

Table 29      Attempted Cyclisation of Alkenes

Alkene	Complex	Product	Yield	Compound
PB	Pd(OAc) <sub>2</sub> <sup>*</sup>	1	34.0	Isomer of PB
		2	2.0	Not identified
		3	1.0	Cyclised product
PB <sup>†</sup>	Pd(OAc) <sub>2</sub>	1	11.0	Isomer of PB
		2	1.2	Isomer of PB
		3	1.3	Cyclised product
		4	1.0	Acetoxyated alkene
PB	Pd(OCOEt) <sub>2</sub>	1	24.0	Isomer of PB
		2	1.3	Not identified
		3	1.5	Cyclised product
		4	1.0	Acetoxyated alkene

Table 29 (cont)

Alkene	Complex	Product	Yield	Compound
AB	$\text{Pd}(\text{OAc})_2$	1	13.0	Isomer of AB
		2	1.0	Cyclised product
AB	$(\text{PhCN})_2\text{PdCl}_2$	1	1.0	Isomer of AB
APE	$\text{Pd}(\text{OAc})_2$	1	34.0	Not identified
		2	1.0	Not identified
		3	3.6	Cyclised product
APE	$(\text{PhCN})_2\text{PdCl}_2$	1	40.0	Not identified
		2	1.0	Isomer of APE
		3	2.4	APE
		4	34.0	Mainly benzonitrile but <u>ca.</u> 5% cyclised product

\*: Palladium acetate batch 2A. Batch 6A in other acetate reactions.

$t$ : Reaction time 2.5 h. All other reaction times 3h.

## DISCUSSION

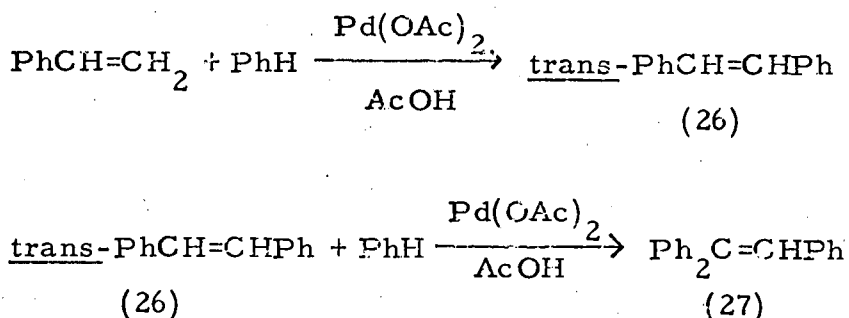
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## 1. PALLADIUM ACETATE

In the phenylation of styrene assisted by palladium (II) acetate both trans-stilbene (26) and triphenylethylene (27) were formed, the former (26) by the phenylation of styrene and the latter (27) by the phenylation of trans-stilbene (26), [Scheme 12].



Scheme 12

It was found that the ratio of trans-stilbene (26) to triphenylethylene (27) varied with different batches of palladium acetate and even with one batch of the acetate. It was decided, therefore, to prepare and purify palladium acetate by various methods to determine whether or not sufficiently pure palladium acetate could be obtained to give consistent results in the phenylation of styrene.

Palladium acetate, therefore, was prepared many times by the Wilkinson method<sup>73</sup> with slight modifications. Samples were purified by various methods. The methods of preparation and purification are described briefly below, but are described more fully in the Experimental section [2.1, p. 27].

### 1.1 Preparation and Purification of Palladium Acetate

#### Preparation

Method (a) Palladium acetate was prepared from palladium sponge by the method of Wilkinson et al.<sup>73</sup>

Palladium sponge, prepared by reduction of palladium (II) chloride with hydrazine hydrate, was added to a mixture of

excess glacial acetic acid and nitric acid and the mixture was heated under reflux until no more brown fumes of nitrogen dioxide were evolved. A small amount of palladium sponge was then added and the mixture again heated under reflux until no more nitrogen dioxide was evolved. The solution was filtered to remove unreacted palladium and was allowed to cool. Palladium acetate precipitated from the cooling solution, was collected by filtration and was dried under high vacuum for 3 h affording palladium acetate (ca. 30% yield).

Method (b) Palladium acetate was prepared by method (a) except that mother liquors from previous palladium acetate preparations were used instead of glacial acetic acid.

Method (c) Palladium acetate was prepared by method (a) except that, when no more brown fumes of nitrogen dioxide were evolved, the reaction mixture was heated under reflux for a further 20 min.

#### Purification of Palladium Acetate

Method I Palladium acetate, prepared by method (a), was recrystallised from benzene.

Method II Palladium acetate, prepared by method (a), was dissolved in warm benzene, the solution being mixed with half its volume of glacial acetic acid, and the benzene was allowed to evaporate slowly at room temperature. The acetate crystallised and was recovered from the solution.

Method III Palladium acetate, prepared by method (a), was washed with cold light petroleum and was then dried over phosphorus pentoxide at 50° for 3 h under high vacuum.

Method IV Palladium acetate, prepared by method (a), was purified by the method of Davidson.<sup>74</sup>

Palladium acetate was ground to a fine powder and was worked into a paste with concentrated sulphuric acid. The paste



was heated to  $135^{\circ}$  for 40 min, cooled and then dissolved in water. Sodium carbonate was added in small portions until some precipitation of palladium acetate occurred. Glacial acetic acid was added and a small crop of palladium acetate was removed by filtration. Addition of a small amount of sodium carbonate followed by addition of glacial acetic acid led to precipitation of palladium acetate. The acetate was collected by filtration and was dried for 3 h under high vacuum.

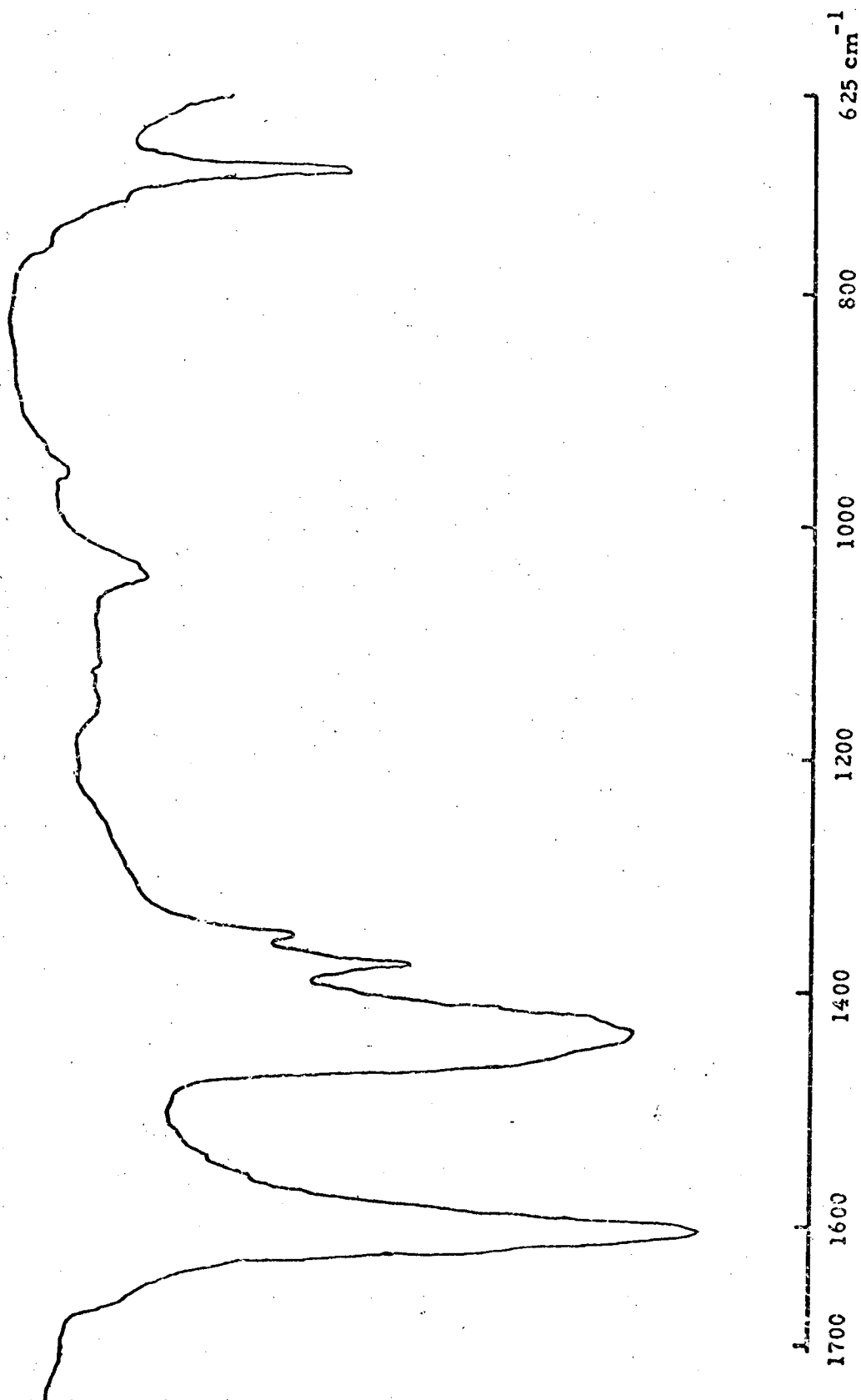
Method V Palladium acetate, prepared by method (c), was dissolved in glacial acetic acid and air was bubbled through the solution which was heated under reflux for 2 h, the acetate being allowed to precipitate from the cooling solution.

Method VI Palladium acetate, supplied by Engelhard Ind. Inc., was recrystallised from glacial acetic acid.

All batches of palladium acetate were checked for physical appearance and underwent elemental analysis. The i. r. spectrum of each batch was run.

When palladium acetate prepared by methods (a), (b) and (c) underwent no purification (batches 2A, 2B, 3A, 3C, 4A, 5A, 6A, 6B, 7, 10 and 11) the acetate was obtained either as a brown powder or as a brown crystalline solid. Correct elemental analyses were obtained only from batches obtained as the first crop of material although correct elemental analyses were not obtained from all such batches.

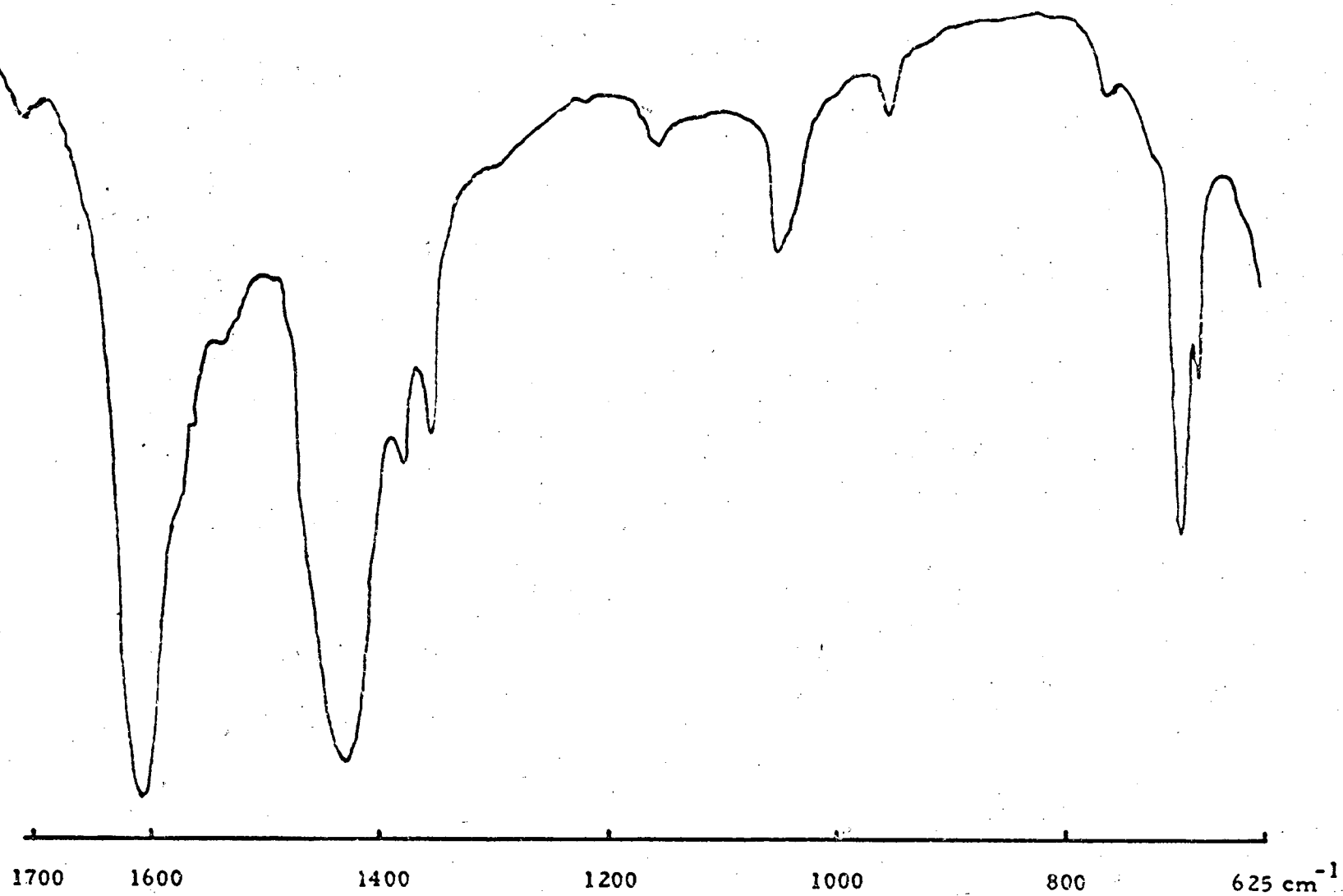
The use of mother liquors from previous palladium acetate preparations instead of glacial acetic acid gave, in all cases, the acetate as a brown powder (batches 6A, 6B and 7) and of the elemental analyses of these batches only one was correct within experimental error. The mother liquors contain both palladium acetate and impurities in solution and so, by using these liquors to prepare more palladium acetate, it would be expected that the amount of impurity in the freshly prepared palladium acetate would be greater than in the acetate prepared originally.



I.R. Spectrum of Palladium Acetate Batch 1

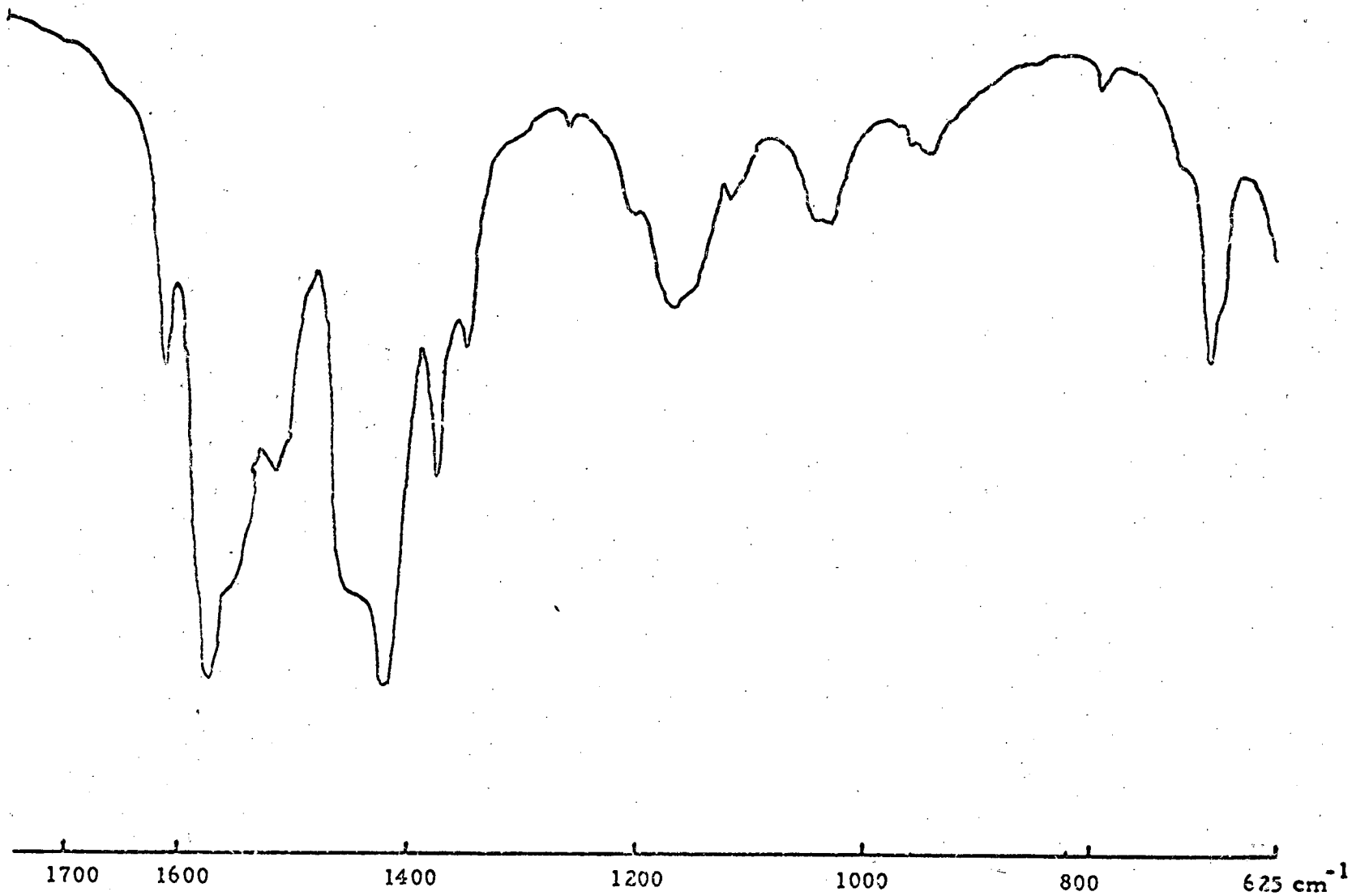
Figure 1a

Figure 1b



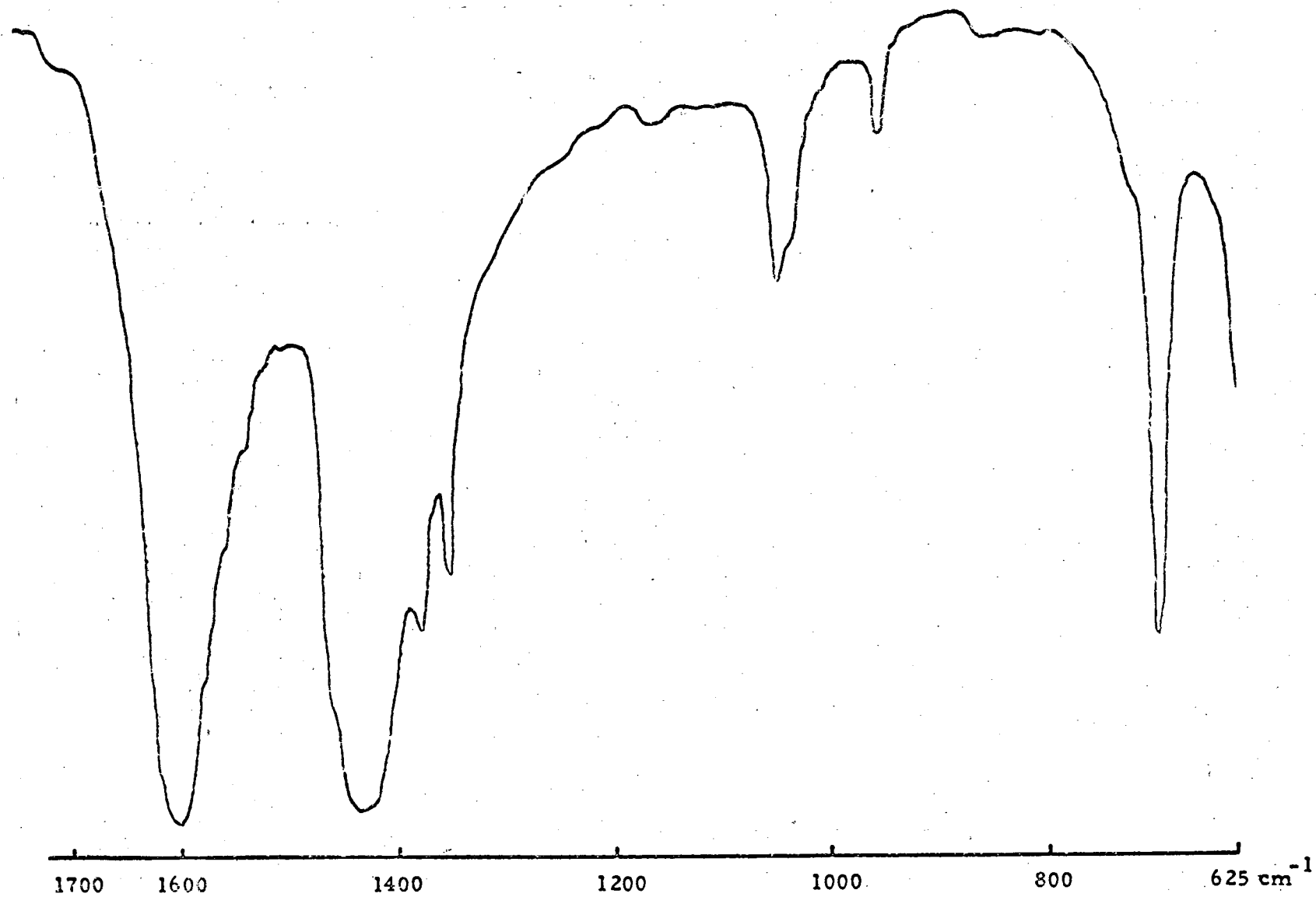
I. r. Spectrum of Palladium Acetate Batch 5B

Figure 1c



I. r. Spectrum of Palladium Acetate Batch 9A

Figure 1d



I. r. Spectrum of Palladium Acetate Batch 11

Method (c) has been used twice without further purification of the product and the acetate was obtained as a brown crystalline solid whose elemental analyses were correct.

The use of the purification methods has not been sufficiently extensive for any definite trends in their effects on the purity of palladium acetate, as determined by elemental analysis and i. r., to have become apparent. However, two methods (II and V) have, in all cases, given a crystalline product although with method II, the elemental analyses were not always correct.

The Davidson purification (method IV) can produce pure palladium acetate.<sup>74</sup> However, difficulties were encountered viz. precipitation of palladium acetate not occurring or precipitation of a reddish-brown solid which has been shown to be very impure.

The sample of palladium acetate used as the i. r. reference sample was batch 1 which was prepared by Davidson by the method of Wilkinson et al.<sup>73</sup> and purified by the Davidson method.<sup>74</sup> This batch was considered by Davidson to be pure. In addition to the assigned absorptions ( $\nu_{\text{max.}}$  ca. 1610, ca. 1440 and ca. 700  $\text{cm}^{-1}$ ) are three weak absorptions ( $\nu_{\text{max.}}$  ca. 1160, 1050 and 955  $\text{cm}^{-1}$ ). Any additional absorptions in the region, 625-1200  $\text{cm}^{-1}$ , are considered to be indicative of impure palladium (II) acetate.

Comparison of the i. r. spectrum of palladium acetate, batch 1, with other batches shows a slight variation in the strengths of these latter absorptions (i. e.  $\nu_{\text{max.}}$  ca. 1160, 1050 and 955  $\text{cm}^{-1}$ ) [Figure 1]. However, it is not possible to identify a batch of palladium acetate, thought pure by elemental analysis, by consideration of the respective strengths of these three weak absorptions.

The best guide to the purity of palladium acetate which can be obtained from the i. r. spectrum is a study of the region 1500-1600  $\text{cm}^{-1}$ . All batches show some additional absorptions in this region but in batches of acetate considered to be pure (eg. 1, 4A, 4E, 9B, 10 and 11) absorptions are seen only as shoulders of the assigned absorption,  $\nu_{\text{max.}}$  1610  $\text{cm}^{-1}$ . Other batches all show prominent

absorptions in the region of the spectrum under study.

Determination of the purity of palladium acetate is best performed by i. r. analysis along with the elemental analysis and consideration of physical appearance. The method is summarised below.

Physical appearance. If the palladium acetate is not brown and crystalline then the sample is unlikely to be pure although brown crystalline samples need not be pure.

Elemental analysis. Analysis for nitrogen should be performed. There should be, of course, no nitrogen present, but some samples were found to contain nitrogen (ca. 1.5%).

I. r. spectrum. The following absorptions should be present;  $\nu_{\text{max.}}$  ca. 1610, 1440 and  $700 \text{ cm}^{-1}$ . Weak absorptions,  $\nu_{\text{max.}}$  ca. 1160, 1050 and  $955 \text{ cm}^{-1}$  should also be present although their respective strengths may vary. Any additional absorptions in the region  $625\text{-}1200 \text{ cm}^{-1}$  and absorptions in the region  $1500\text{-}1600 \text{ cm}^{-1}$ , if prominent, are indicative of impure palladium acetate.

When this procedure is applied to all batches of palladium acetate it is possible to propose tentatively that the purest palladium acetate is obtained by: preparation by method (c) and purification by method V.

Method (c) was used four times, including twice with purification method V, and in all four cases the i. r. spectrum and elemental analysis obtained are those of pure palladium acetate, according to the criteria described above.

No investigation into identification of the impurities in palladium acetate was carried out but several reports in the literature suggest what these impurities may be.

Braithwaite and Wright<sup>80</sup> found that reaction of palladium (II) acetate with lithium nitrate trihydrate (10-fold excess) in boiling glacial acetic acid afforded acetatocyanopalladium (II). This complex was not formed with nitric acid, probably because acetate ion is removed from solution by nitric acid. However, in the Wilkinson

preparation of palladium acetate<sup>73</sup> a vast excess of glacial acetic acid is used and so formation of the cyano-complex may occur. No i. r. absorption corresponding to the presence of cyanide is present in any batch of palladium acetate but an absorption due to acetate ( $\nu_{\text{max.}} 1582 \text{ cm}^{-1}$ ) was found with several batches.

Addison and Ward<sup>81</sup> identified the product, obtained from a solution of palladium metal in nitric acid, as the palladium (IV) complex,  $[\text{Pd}(\text{NO}_3)_2(\text{OH})_2]$ . This complex could also be formed during the preparation of palladium acetate because nitric acid is involved, although from i. r. spectrum analysis there is no evidence for nitrate ion.

Wilkinson *et al.*<sup>73</sup> reported formation of a nitrogen dioxide complex of palladium,  $[\text{Pd}(\text{NO}_2)\text{OAc}]$ , if, in their palladium acetate formation, boiling of the reaction mixture were stopped before all the brown fumes of nitrogen dioxide were evolved.

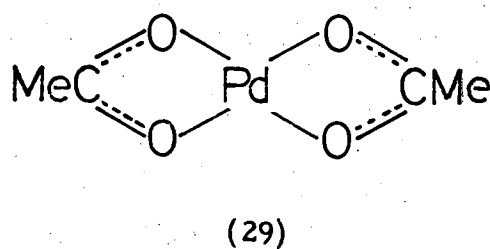
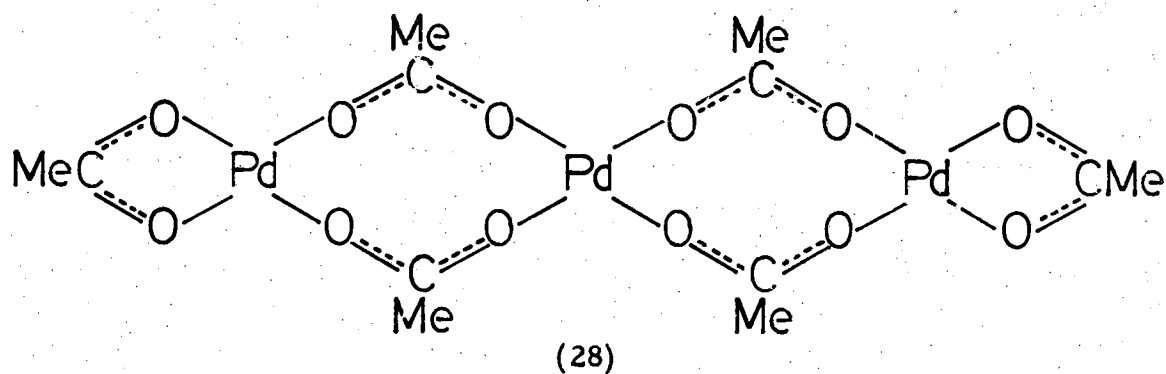
Wolfe and Campbell,<sup>82</sup> who investigated the disproportionation of cyclohexene to cyclohexane and benzene in the presence of acetic acid and palladium acetate, observed that the presence of a small amount of nitric or nitrous acid favoured acetoxylation of the alkene. They suggested that a small amount of nitrate or nitrite impurity might well affect the rate of reaction, and, indeed, the actual reaction which occurs.

## 1.2 Structure of Palladium (II) Carboxylates

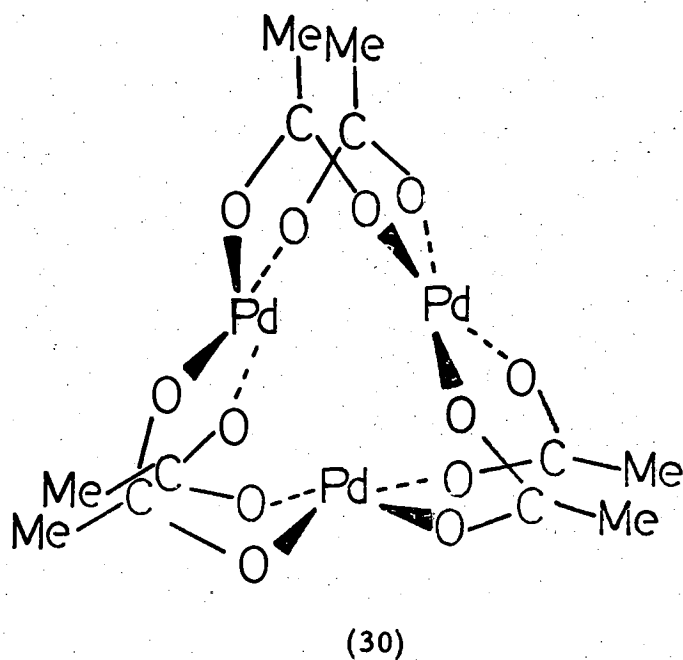
Wilkinson and co-workers<sup>73</sup> found palladium (II) acetate and palladium (II) propionate to be trimeric in benzene at  $37^\circ$  and monomeric in benzene at  $80^\circ$ . Attempts to study the trimer-monomer equilibrium by high-resolution n.m.r. spectral measurements failed because the spectra of the two species appeared to show no features that were characteristic, only a single peak being found. Palladium (II) benzoate was found to be trimeric in benzene both at  $37^\circ$  and  $80^\circ$ . Wilkinson suggested that in palladium (II) acetate, the palladium atom has its normal four coordinate square planar configuration, the



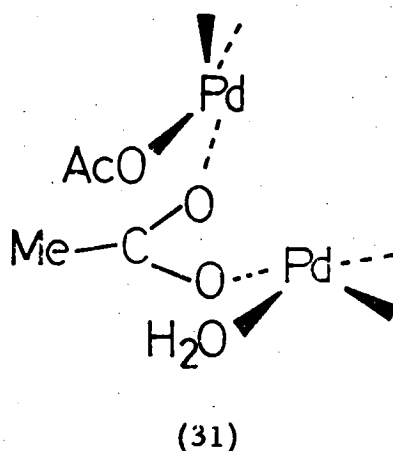
trimer (28) having both bridging and chelating groups and the monomer (29) having only chelating groups.



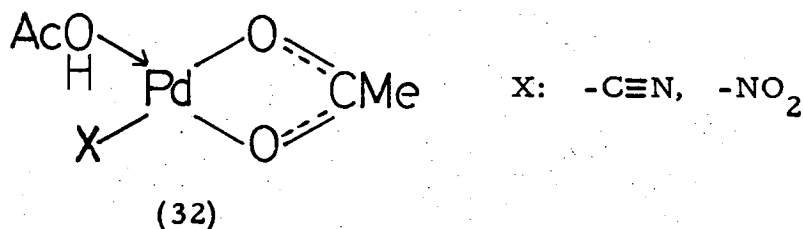
However, Skapski and Smart<sup>83</sup> showed the solid to be a trimeric cluster (30).



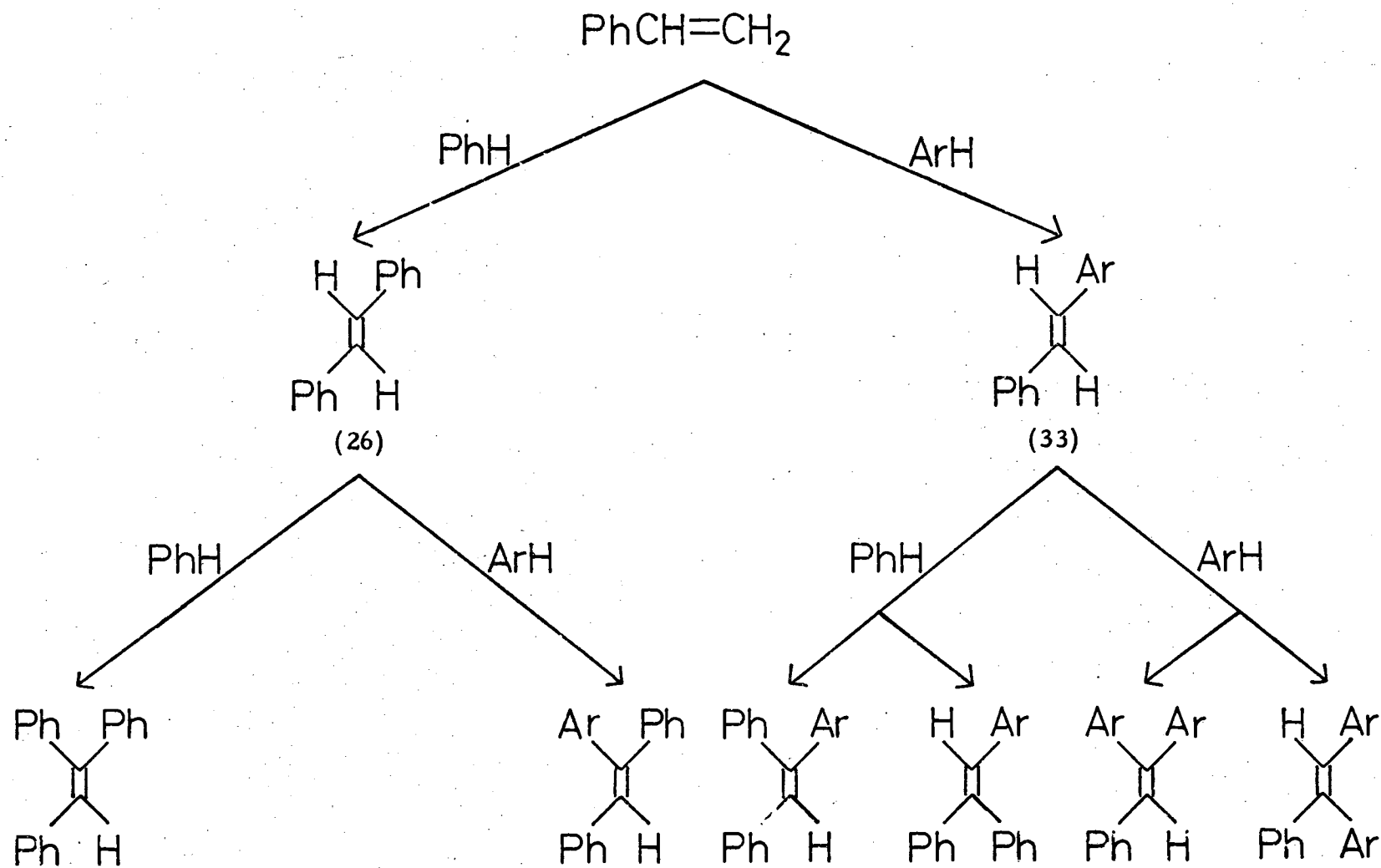
Eberson and Gomez-Gonzalez<sup>84</sup> attempted to gain an insight into the structure and composition of palladium (II) acetate under the reaction conditions of their aromatic acetoxylation, acetic acid being the solvent, by the use of n.m.r. spectroscopy. They suggested that in solution at room temperature in the presence of a small amount of water a palladium-to-oxygen (in acetate) bond in (30) is broken by a water molecule to give a species (31) (only two of the three palladium atoms being shown).



A similar mechanism is possible for the incorporation of a cyano- or nitro-group into palladium (II) acetate thus explaining the possible formation of the impurities mentioned previously. However, under the conditions of styrene phenylation assisted by palladium acetate (77°) the acetate and presumably the impurity are monomeric, the impurity probably having a structure (32) as shown.



Because the mechanisms proposed for styrene phenylation [benzene in 100-fold excess relative to both styrene and palladium acetate] suggest that a palladium-to-oxygen (in acetate) bond is broken and that a carbon-palladium  $\sigma$ -bond is formed, the presence



Scheme 13

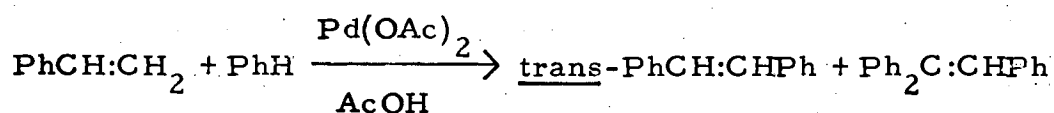
of impurity X, (32) in the fourth coordination site would be expected to affect the rate at which the alkene or arene is capable of forming a  $\sigma$ -bond with palladium. The variation in the trans-stilbene to triphenylethylene ratio obtained in the phenylation of styrene is explicable on this basis.

### 1.3 Phenylation of Styrene Assisted by Palladium (II) Acetate.

Several competitive arylations of styrene with benzene and a substituted benzene assisted by palladium acetate were carried out and the yields of trans-stilbene (26) and substituted trans-stilbene (33) were determined by g.l.c. However, it was found that both stilbenes, (26) and (33), could also react with benzene or substituted benzene to give several triarylethylenes, [Scheme 13], yields of which could not be determined by g.l.c. because of incomplete separation.

Because of this further arylation no conclusions can be drawn from a comparison of the yields of mono-arylated products, (26) and (33). An investigation into the phenylation of styrene assisted by palladium acetate (batch 2A), [benzene being in 100-fold excess relative to both styrene and palladium acetate] was performed, therefore, in order to gain a better understanding of the basic reaction. The results are recorded in Table 7. Since triphenylethylene is formed by phenylation of stilbene, the total yield of stilbene is obtained by addition of the yields of stilbene and triphenylethylene. The total consumption of palladium is obtained by addition of the triphenylethylene yield to the total yield of stilbene because two moles of palladium acetate are required to produce one mole of triphenylethylene. The results in Table 7 show that trans-stilbene is formed in about 50 per cent yield but that varying amounts of stilbene react with benzene to give triphenylethylene.

Because of the inconsistency in the results in styrene phenylation as shown in Table 7 it was necessary to perform a

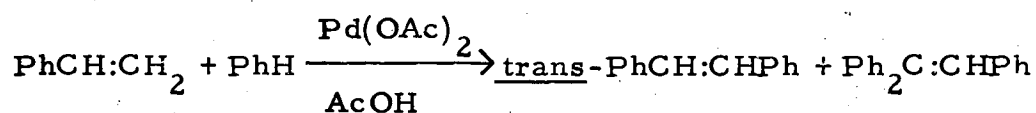
Table 7 Palladium Acetate Assisted Phenylation of Styrene.Palladium Acetate Batch 2A.

Stilbene (%)	TPE (%)	Total Stilbene (%)	Total Reaction of Palladium (%)
32.3	20.4	52.7	73.1
51.1	3.5	54.6	58.1
52.7	9.5	62.2	71.7
39.7	14.3	54.0	68.3
2.0	40.0	42.0	82.0

TPE:- triphenylethylene

comparison of the effect of different batches of palladium acetate in this reaction and Table 8 illustrates the results obtained.

Table 8 Product Distribution Obtained from the Palladium Acetate Assisted Phenylation of Styrene. Various Batches of Palladium Acetate



Pd(OAc) <sub>2</sub> Batch	Stilbene (%)	TPE (%)	Total Stilbene (%)	Total Reaction of Palladium (%)
1	8.0	55.0	63.0	118.0
1	25.6	38.8	64.4	103.2
2A	51.1	3.5	54.6	58.1
2A	52.7	9.5	62.2	71.7
4E	11.5	64.5	76.0	140.5
9B	12.1	52.8	64.9	117.7

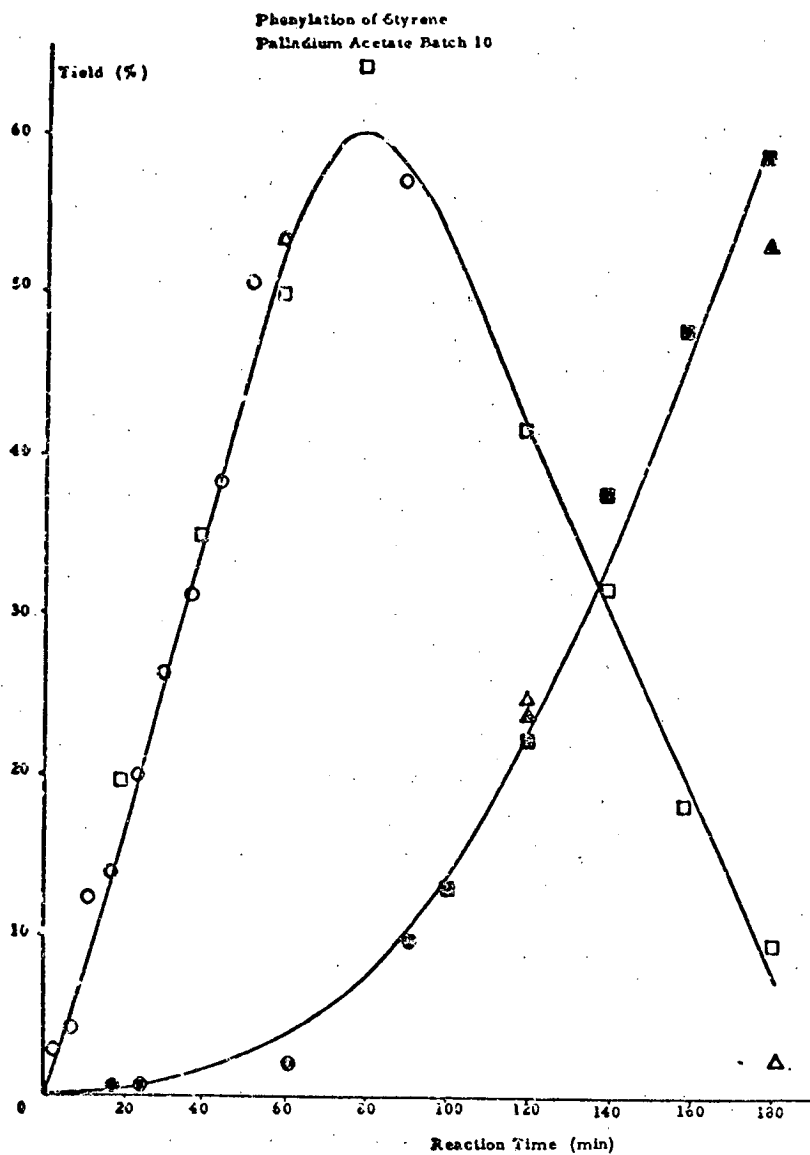
Table 8 (cont.)

Pd(OAc) <sub>2</sub>		Total		Total Reaction
Batch	Stilbene (%)	TPE (%)	Stilbene (%)	of Palladium (%)
9B	36.0	37.0	73.0	110.0
9B	6.2	60.5	66.7	127.2
9B	3.7	65.0	68.7	133.7
10	25.4	45.8	71.2	117.0
10	53.7	21.3	75.0	96.3
11	25.7	42.0	67.7	109.7
11	21.7	46.7	68.4	115.1
11	19.2	49.4	68.6	118.0
11	21.0	44.8	65.8	110.6

TPE:- triphenylethylene

The results in Table 8 show that diarylation (that is phenylation of stilbene formed to afford triphenylethylene) occurred to a considerable extent with all batches of palladium acetate used except batch 2A. In the majority of reactions, yields of triphenylethylene greater than 40 per cent were observed, the total yield of stilbene being in the range 54 to 75 per cent [cf. Table 7 p. p.69]. Another point worthy of note is that the total reaction of palladium is, in most cases, greater than 100 per cent and so palladium (0), produced during the reactions, is re-oxidised to palladium (II) presumably by air.

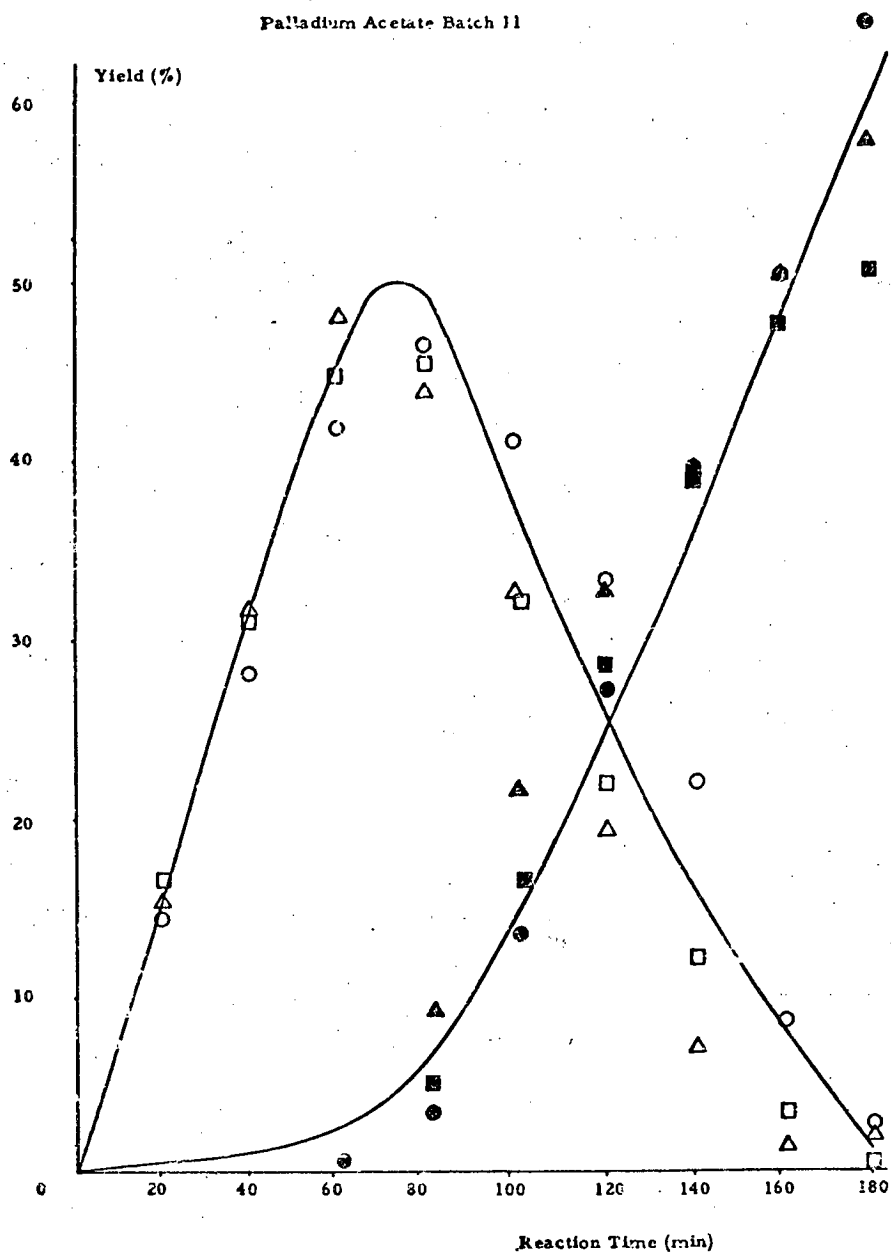
It is now worth comparing Tables 7 and 8 with results reported by Moritani and co-workers.<sup>14, 15</sup> They found from separate experiments that the conversion of styrene into trans-stilbene occurred in 90 per cent yield and also that conversion of trans-stilbene into triphenylethylene occurred in 28 per cent yield. However, formation of triphenylethylene in the phenylation of styrene was not observed. The only mention of diarylation reported by



1	2	3	
○	□	△	<u>trans</u> -stilbene
●	■	▲	triphenylethylene

Figure 2A

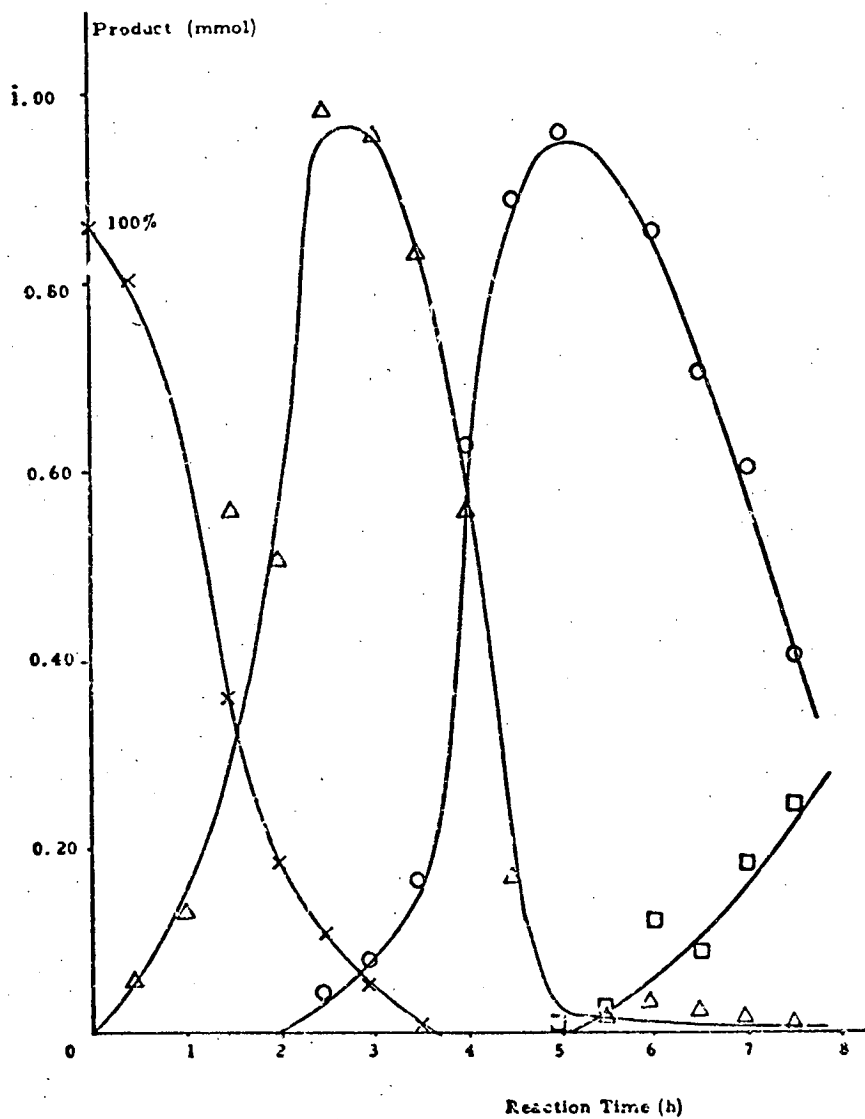
Phenylation of Styrene  
Palladium Acetate Batch 11



1	2	3	
○	□	△	<u>trans</u> -stilbene
●	■	▲	triphenylethylene

Figure 2B





- X styrene (ordinate in % initially charged)
- Δ trans-stilbene
- O triphenylethylene
- tetraphenylethylene

Figure 10

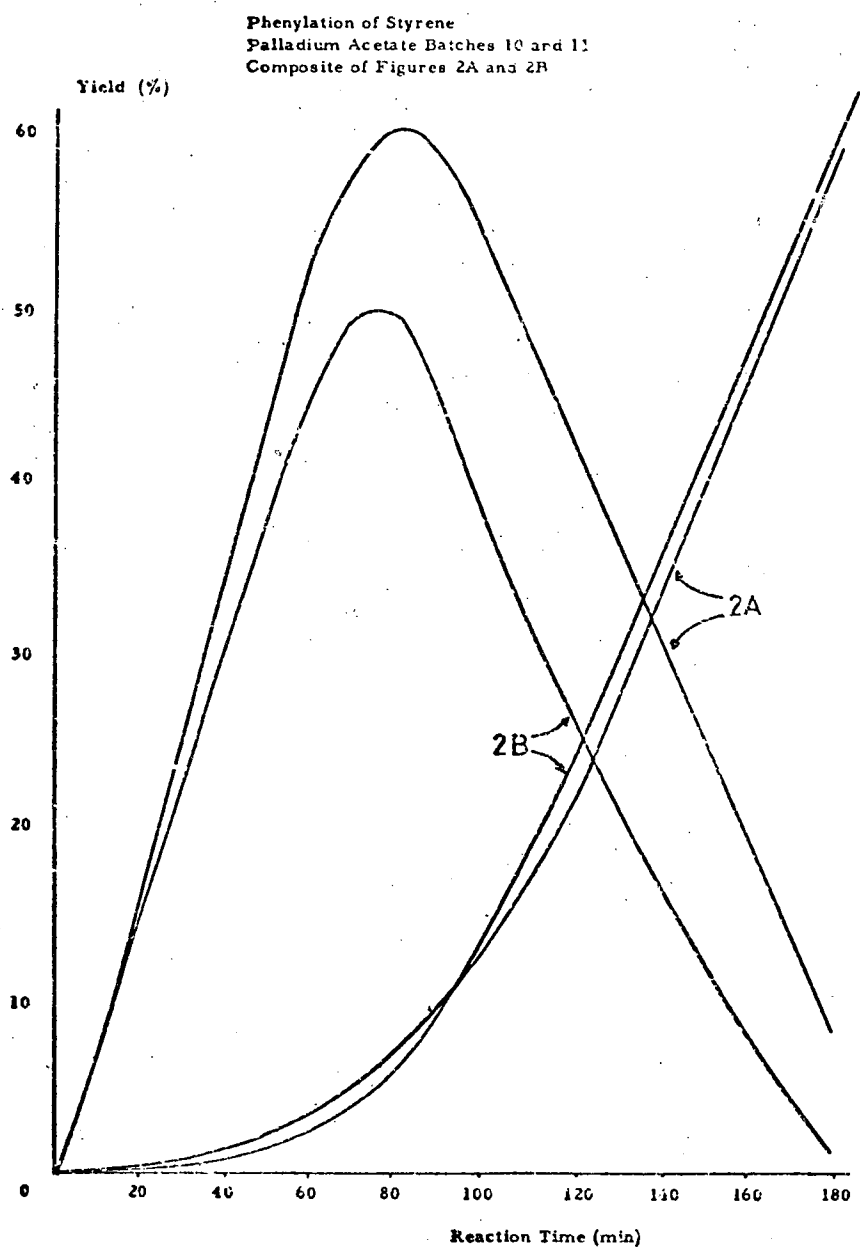


Figure 11

Moritani *et al.*<sup>15</sup> was in the reaction of ethylene with either benzene or toluene with the yields of diarylated product being about 4 per cent and 5 per cent respectively.

Because, in the present study, diarylation occurred to such a great extent, a kinetic study of the phenylation of styrene in the presence of palladium acetate became necessary and this was carried out under reaction conditions (3) at 77°. The appearance and subsequent disappearance of trans-stilbene, and the appearance of triphenylethylene were determined by g.l.c. analysis. The results are illustrated in Figure 2, the graphs representing the results obtained with palladium acetate, batches 10 and 11. Both graphs show that arylation of trans-stilbene becomes important only when the yield of trans-stilbene is large (greater than 50. per cent).

Shue<sup>43</sup> reported the rate of styrene phenylation to be sufficiently high, relative to the rate of stilbene phenylation, that further arylation to produce triphenylethylene and tetraphenylethylene was negligible unless the styrene concentration reached essentially zero. This was illustrated by a graph of product distribution versus reaction time in the phenylation of styrene [Figure 10]. This Figure shows that only when the yield of trans-stilbene is large does further phenylation to triphenylethylene become important and a similar trend is observed for tetraphenylethylene formation from triphenylethylene. Figure 2, obtained from the current work, and Figure 10, reported by Shue are similar. Shue fails to record that, after different induction periods, the rates of trans-stilbene and of triphenylethylene formation are not greatly different.

Figure 2 was obtained from the phenylation of styrene, each reaction being carried out three times with palladium acetate, batches 10 and 11. Agreement of the yields of trans-stilbene, obtained with each batch, is good until triphenylethylene formation becomes important.

Figure 11 shows that agreement of the trans-stilbene yield with different batches of palladium acetate (10 and 11) is good during

Arylation of Styrene with *p*-Xylene  
Palladium Acetate Batches 10 and 11  
Composite of Figures 3A and 3B

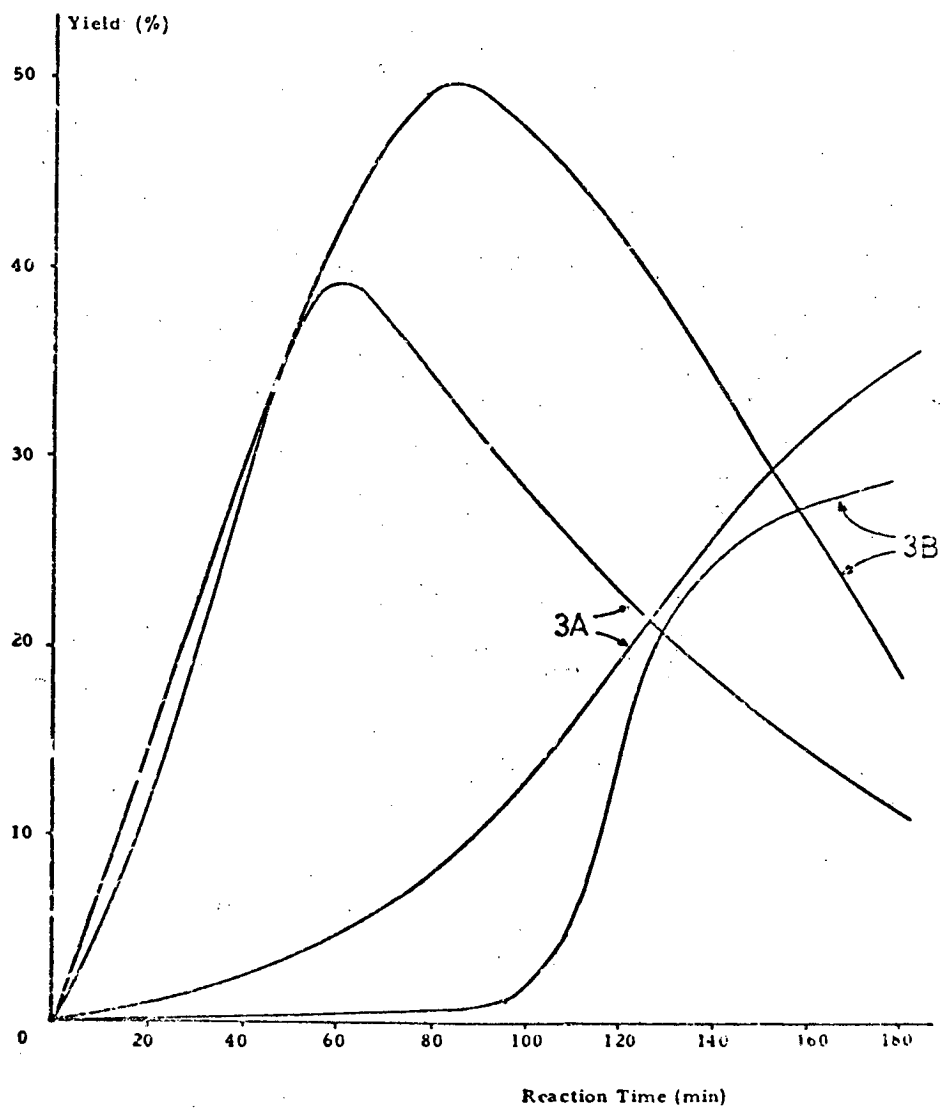


Figure 12

the initial forty minutes of reaction, that is when formation of triphenylethylene is small (less than 2.5 per cent). These results suggest that phenylation of styrene to trans-stilbene can be studied reliably by observing the reaction over an initial period of about forty minutes.

#### 1.4 Arylation of Styrene Assisted by Palladium (II) Acetate

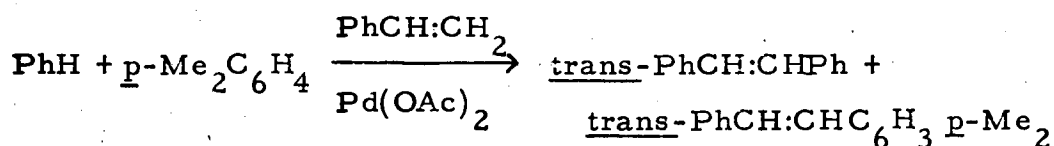
It is important that arylation of styrene with substituted benzenes should also be capable of reliable study and, to this end, a kinetic study of the arylation of styrene with *p*-xylene was carried out with palladium acetate, batches 10 and 11. Figure 12 illustrates the relationship between product distribution and reaction time for this reaction. As for the styrene phenylation already discussed, the extent of arylation of the initially formed stilbene is small (less than 3 per cent) over an initial reaction time of forty minutes. Over the same period, different batches of palladium acetate give similar yields of 2,5-dimethyl-trans-stilbene. However, agreement is poorer at reaction times greater than forty minutes.

It is now possible to perform competitive arylations of styrene, in the knowledge that, over the initial period of forty minutes the yields of trans-stilbene and substituted trans-stilbene are virtually unaffected by further arylation and so any calculations based on these yields are more accurate than those carried out previously.

#### 1.5 Competitive Arylation of Styrene Assisted by Palladium (II) Acetate

A series of competitive arylations of styrene with benzene and *p*-xylene in the presence of several batches of palladium acetate was carried out to confirm that consistency of results was possible. Table 11 lists the product distribution, and the variations in the partial rate factor of *p*-xylene and in the reactivity ratio of *p*-xylene to benzene, ( $k_X/k_H$ ), with change of reaction time and of batch of palladium acetate.

**Table 11**      Competitive Arylation of Styrene with Benzene and p-Xylene with various Batches of Palladium Acetate



Pd(OAc) <sub>2</sub> Batch	Stilbene (%)	Substituted Stilbene (%)	Partial Rate Factor	Reactivity Ratio ( $k_X/k_H$ )
6B	6.0	9.0	2.26	1.51
6B	6.8	8.8	1.94	1.29
11	8.0	11.0	2.09	1.39
11	9.2	13.1	2.15	1.43
11	8.5	12.0	2.10	1.40*
14A	9.9	11.6	1.75	1.17
14A	8.0	11.8	2.21	1.47
14B	8.2	11.8	2.16	1.44
14B	8.3	12.3	2.22	1.48
9B	15.4	22.4	2.18	1.46 <sup>†</sup>
9B	11.4	16.5	2.18	1.45 <sup>†</sup>
10	12.4	15.2	1.83	1.22 <sup>†</sup>
10	12.0	14.9	1.87	1.25 <sup>†</sup>
11	12.7	15.7	1.85	1.23 <sup>†</sup>
11	18.2	22.6	1.86	1.24 <sup>†</sup>

\* Reaction carried out under an atmosphere of nitrogen

<sup>†</sup> Reaction time 45 min. All other reaction times 30 min.

When the reaction time was 30 minutes, six of the eight reactions give consistent results for partial rate factor and reactivity ratio. For a reaction time of 45 minutes, palladium acetate, batches 10 and 11, also give consistent results although change of reaction time affects the reactivity ratio and partial rate factor. The variation in partial rate factor and reactivity ratio with reaction

time can be explained by considering a hypothetical situation in which a substituted benzene reacts with styrene more quickly than does benzene [Figure 13].

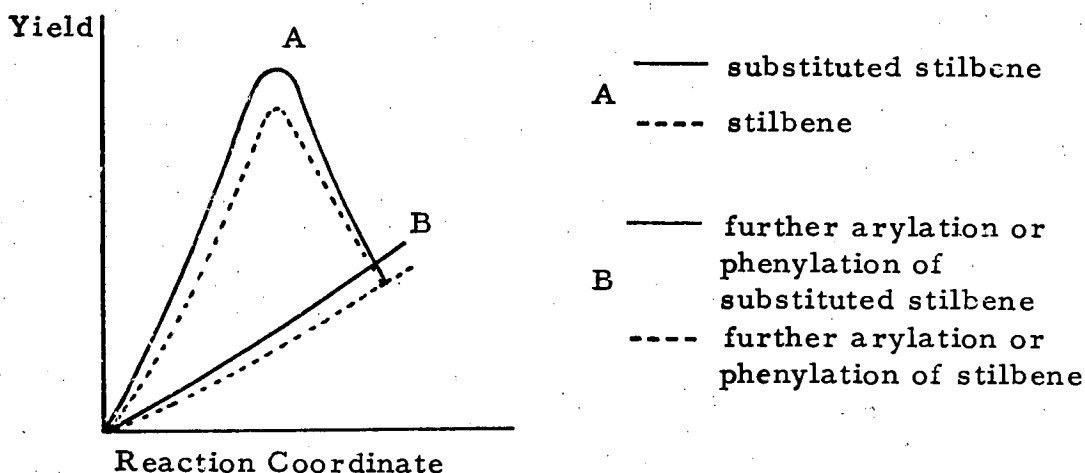


Figure 13

The substituted benzene reacts with styrene more quickly than does benzene and so substituted stilbene is formed more quickly than trans-stilbene. Both stilbene and substituted stilbene can then react with either benzene or substituted benzene and if it is assumed that further phenylation or arylation of the stilbenes is equally facile then further reaction of the substituted stilbene will occur more quickly than that of stilbene. This continues until equal amounts of both stilbene and substituted stilbene remain at which point further reaction of both stilbenes would occur at the same rate. Because the reaction mixture is analysed only for stilbene and substituted stilbene the reduction in the yield of substituted stilbene due to further reaction will be greater than the reduction in the yield of stilbene due to further reaction. Therefore, with increasing reaction time, until the yields of both stilbenes become equal, the apparent reactivity of substituted benzene relative to benzene will decrease.

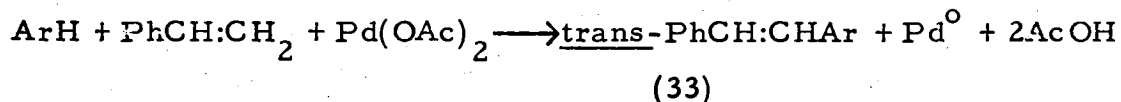
Palladium acetate, batches 11 and 14B give consistent results over a reaction time of 30 minutes and batches 10 and 11 give consistent results over 45 minutes, that is batches of palladium acetate prepared by method (c) or purified by method VI. No batches of the acetate purified by method V were used in these competitive arylations but it is expected that such batches would give results consistent with batches mentioned above because methods V and VI are identical except that in method V recrystallisation was carried out after air was bubbled through the solution.

This work has therefore demonstrated that batches of palladium acetate giving consistent results can be prepared and so it is now possible to investigate the mechanism of palladium acetate assisted arylation of alkenes.

## 2. MECHANISTIC INVESTIGATIONS OF PALLADIUM (II) - ASSISTED ARYLATION OF ALKENES

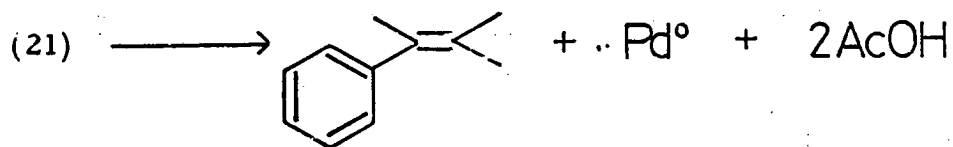
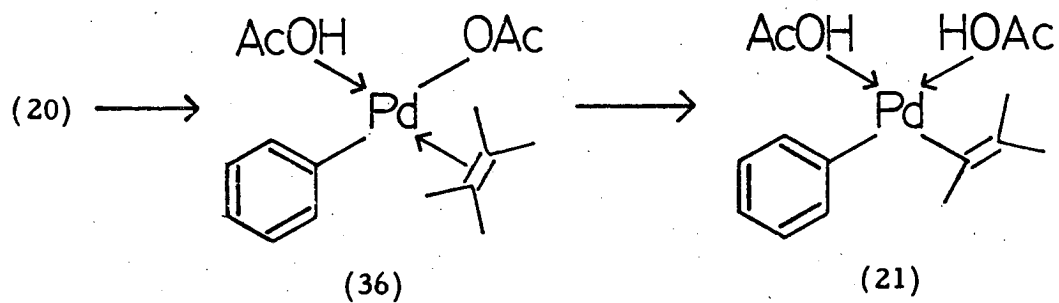
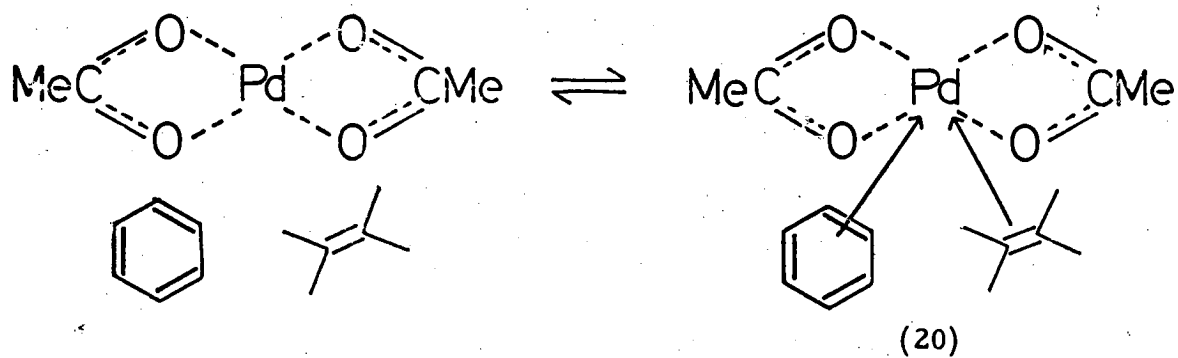
Much work has already been carried out to elucidate the mechanism of palladium (II)-assisted arylation of alkenes, by Moritani<sup>10-29</sup>, Heck<sup>30-40</sup>, Shue<sup>41-43</sup> and Boyd<sup>48</sup>. Workers in other fields have suggested possible mechanisms for alkene arylation by analogy. However the mechanism was still open to doubt at the outset of this investigation.

Palladium (II)-assisted arylation of alkenes is an oxidative coupling reaction of an alkene with an aromatic compound in which the hydrogen lost from each coupling site appears in acetic acid and in which palladium (II) is reduced to palladium (0). The reaction is represented as shown, for the arylation of styrene in the presence of palladium (II) acetate to give a substituted trans-stilbene (33).



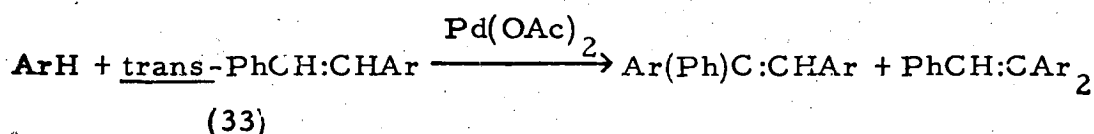
Side reactions are possible, however. The stilbene formed



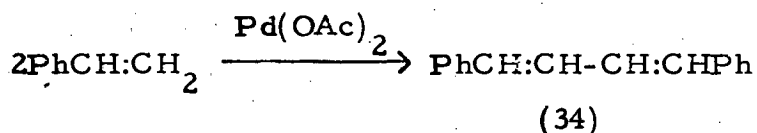


Scheme 10

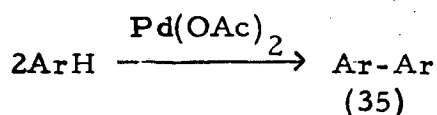
(33) can react with more aromatic compound to afford two disubstituted triphenylethylenes. Alternatively the starting alkene can



be oxidatively coupled to give the dimer. With styrene the product of coupling is 1,4-diphenylbuta-1,3-diene (34). Both of those side



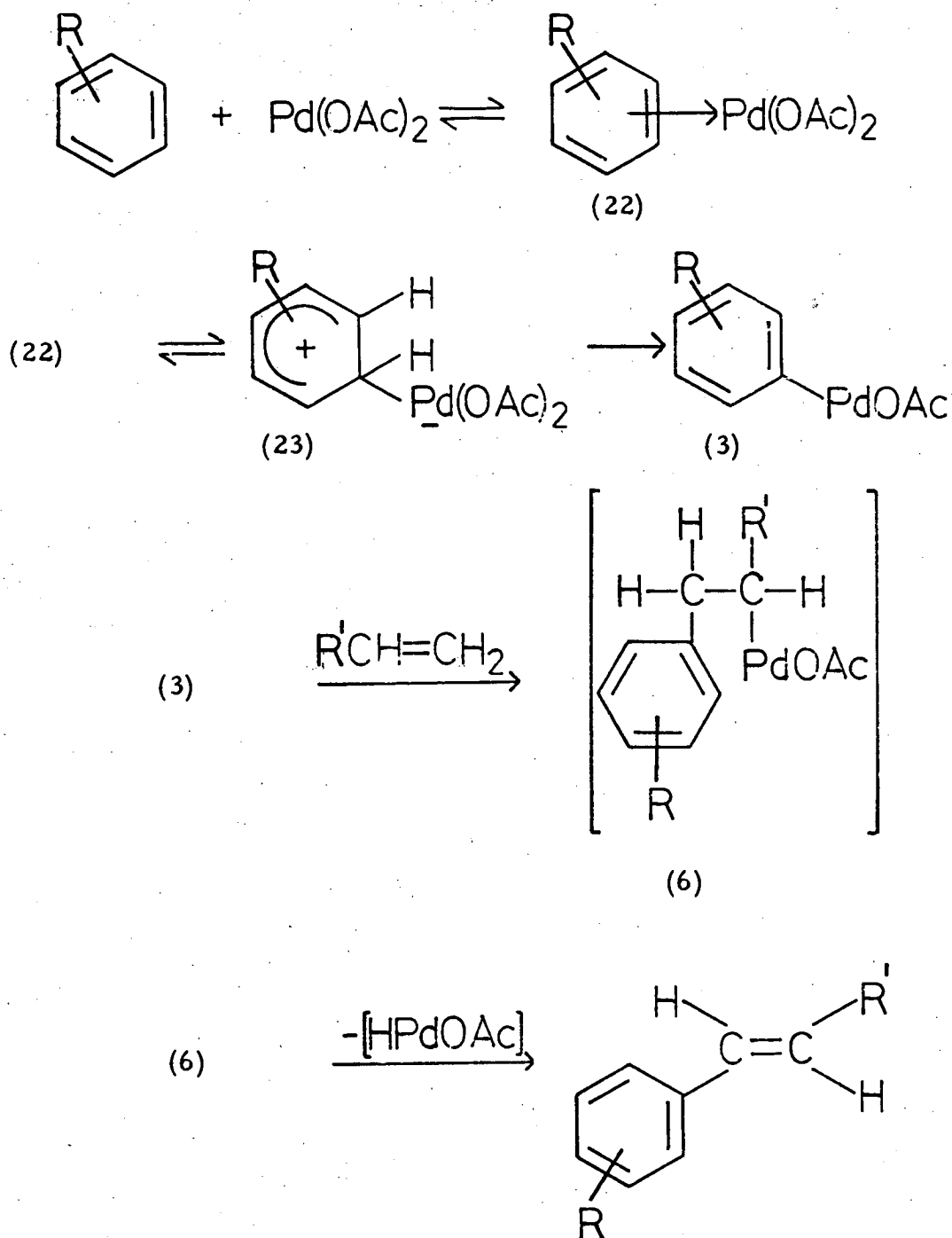
reactions have been observed.<sup>15, 43</sup> Another side reaction which would be expected is oxidative coupling of the aromatic compound to give the biaryl (35). The formation of biaryl (35) has neither



been observed in the present study nor by Boyd.<sup>48</sup>

The mechanism for the arylation of an alkene must be compatible with the occurrence of the two observed side reactions. Only two mechanisms have been proposed; one by Moritani and colleagues<sup>17</sup> and the other, a composite mechanism, proposed in part by Heck<sup>39, 40</sup> and Boyd.<sup>48</sup>

Moritani's proposal is that formation of a  $\sigma$ -bond between alkene and palladium is the rate-determining step. The mechanism is outlined in Scheme 10. Both the alkene and the aromatic compound coordinate with palladium acetate to form a double  $\pi$ -complex (20) which proceeds to a double  $\sigma$ -complex (21) which then decomposes into product alkene, palladium metal and acetic acid. The rate-determining step was postulated as that in which  $\sigma$ -bond formation between the alkene and palladium occurred giving intermediate (21) from species (36). This was based on the variation of reactivity shown by substituted alkenes<sup>16, 18</sup> and the lack of variation of reactivity exhibited by the aromatic compound.<sup>17</sup> However, doubt



Scheme 14

has been cast on this mechanism by Shue's work with deuterated and non-deuterated benzenes<sup>42</sup> which indicated that  $\sigma$ -bond formation between the alkene and palladium was not rate-determining, and by Boyd<sup>48</sup> and later by Moritani himself,<sup>61</sup> all of whom found that substituents in the aromatic compound did, in fact, affect the reactivity.

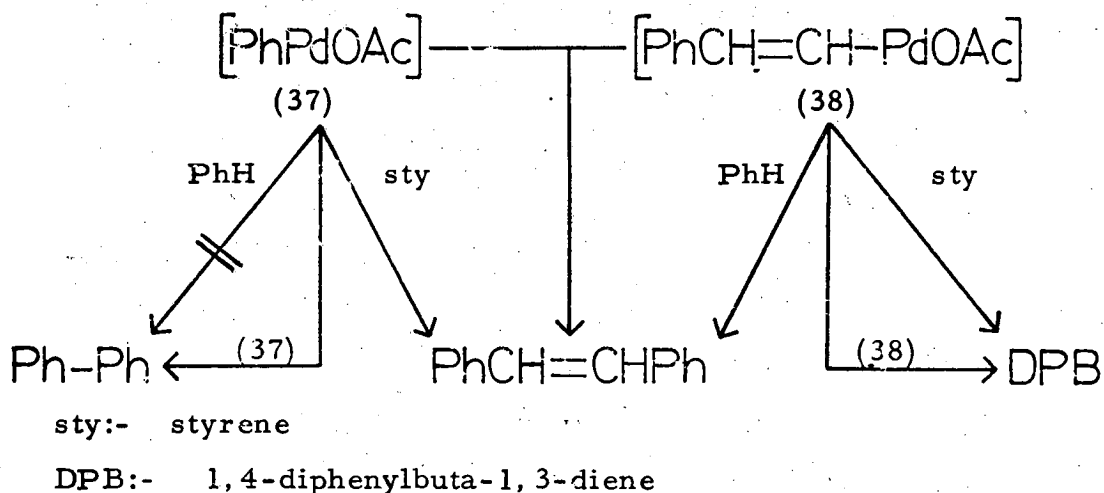
The combined mechanism proposed by Heck<sup>39, 40</sup> and Boyd,<sup>48</sup> [Scheme 14], is one in which the rate-determining step involves  $\sigma$ -bond formation between the aromatic compound and palladium. Reversible formation of a  $\pi$ -arene-palladium complex (22) is the first step, subsequent aryl carbon to palladium  $\sigma$ -bond formation giving intermediate (23) which undergoes non-reversible rate-determining loss of a proton from the aromatic ring, and of an acetate group from palladium to form the  $\sigma$ -arylpalladium acetate (3). cis-Addition of intermediate (3) across the olefinic double bond and cis-elimination of hydridepalladium acetate from adduct (6) affords the arylated alkene.

Of the mechanisms proposed for palladium-assisted arylation of alkenes it is Heck's which is considered by other workers to give a true representation of the reaction. However, in this discussion the intermediacy of a  $\sigma$ -arylpalladium complex is not assumed and the possibility of the reaction proceeding via a  $\sigma$ -alkene-palladium complex is also considered.

Scheme 15 illustrates the formal reaction pathways when intermediacy of a  $\sigma$ -phenylpalladium complex (37) or a  $\sigma$ -styryl complex (38) or both are considered in the phenylation of styrene. It is thought, however, that it is entirely feasible to propose intermediacy only of the  $\sigma$ -styrylpalladium complex (38) in the oxidative coupling of styrene to produce 1,4-diphenylbuta-1,3-diene.

Triphenylethylene can be formed by reactions similar to those producing stilbene.

Since the possible intermediacy of a  $\sigma$ -arylpalladium species and a  $\sigma$ -alkenylpalladium is proposed it is necessary to provide

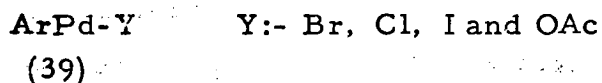


Scheme 15

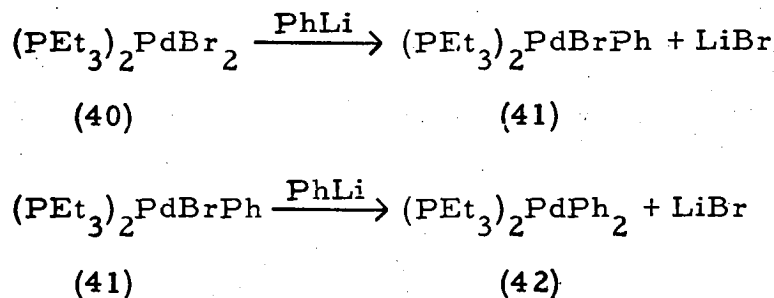
evidence for the existence of each species.

## 2.1 Evidence for the Existence of Arylpalladium Complexes

The intermediacy of a  $\sigma$ -bonded arylpalladium (II) complex (39) has been proposed for a number of reactions<sup>7, 8, 9, 39, 40, 45, 48, 54, 55, 56, 58, 60, 85, 86, 87</sup> but its formation has not been proved.

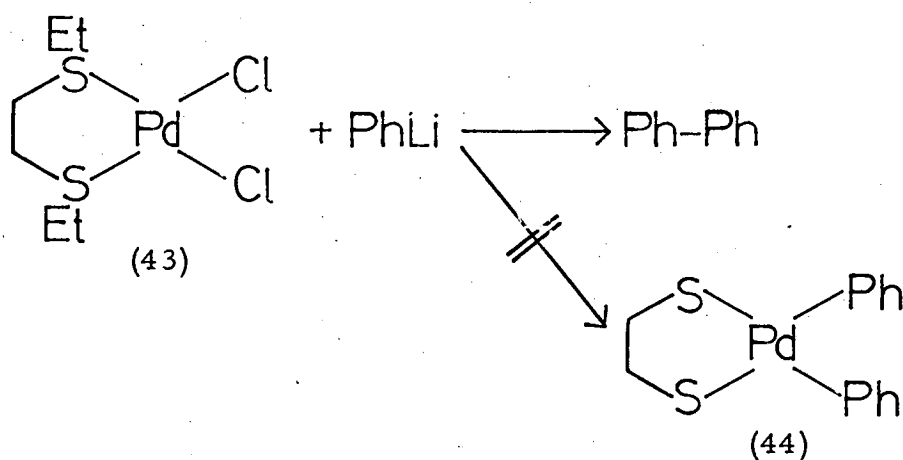


Formation of complexes containing an aryl-carbon to palladium  $\sigma$ -bond was reported in 1960 by Calvin and Coates.<sup>88, 89</sup> Complex halides, usually containing tertiary phosphines, were reacted with Grignard or organolithium compounds to form methyl- or arylpalladium complexes, [Scheme 16].



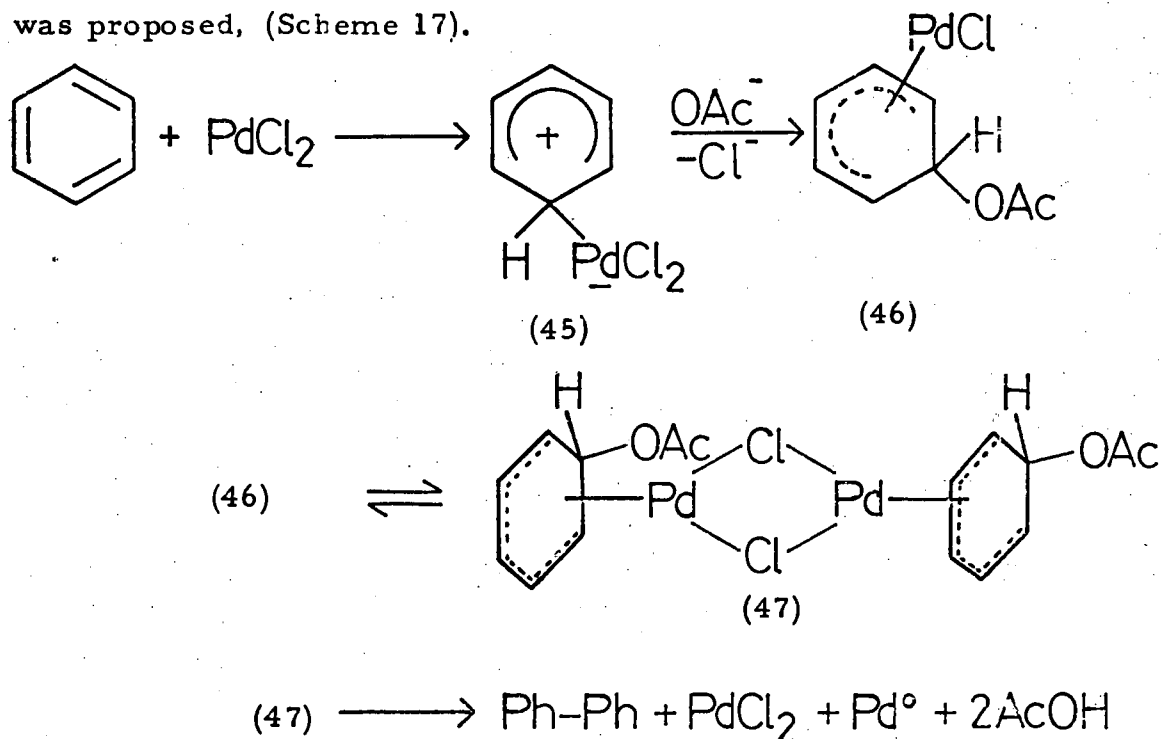
Scheme 16

Thus bis(triethylphosphine)dibromopalladium (II) (40), reacts with phenyllithium to give successively the monophenyl (41) and diphenyl (42) complexes. The former complex (41) is the more stable in accord with the general trend that monoaryl complexes are more stable than diaryl complexes. In a preliminary report,<sup>88</sup> Calvin and Coates described the diphenyl complex (42) as being fairly stable to heat in vacuo. However, on heating in air the complex decomposed to give biphenyl and palladium metal. Only the trans-isomer of such complexes was found, it being suggested that there existed a low energy gap between the ground state of the cis-diphenyl complex and the transition state leading to biphenyl formation and decomposition of the complex. This explains the formation of biphenyl from a complex already held in the cis-conformation (43), instead of the expected product, the cis-diphenyl-palladium complex (44).



The first proposal of the intermediacy of a  $\sigma$ -bonded arylpalladium complex was by van Helden and Verberg<sup>7</sup> who studied the aromatic coupling reaction which occurs on treatment of aromatic compounds with palladium chloride and sodium acetate [1:5] in acetic acid at 90°. In the absence of acetate no reaction occurred. The isomer distribution of biaryls was characteristic of an electrophilic aromatic substitution and a mechanism involving intermediacy of a  $\sigma$ -bonded arene-palladium chloride complex (45)

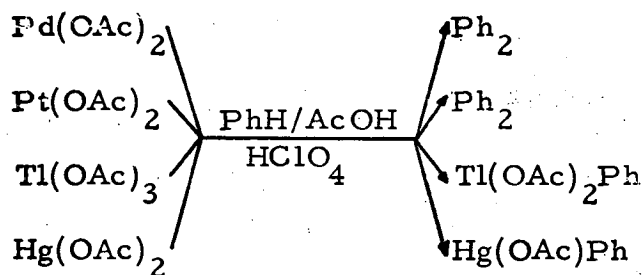
was proposed, (Scheme 17).



Scheme 17

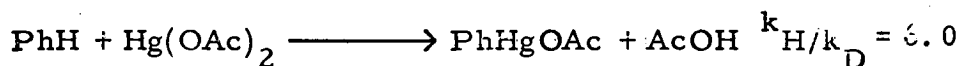
Electrophilic attack by palladium chloride on the aromatic ring to form  $\sigma$ -complex (45) is envisaged as being rate-determining. Fast reaction of (45) with acetate ion affords the  $\pi$ -cyclohexadienyl complex (46) which dimerises to a binuclear complex (47), breakdown of which yields biphenyl. However compounds with bonding similar to (47) have been found not to dimerise<sup>90, 91</sup> and so doubt was cast on this mechanism.

Davidson and Triggs<sup>8, 9</sup> reported the results of a study of the reaction of transition metal acetates with benzene in the presence of acetic acid and perchloric acid. They found that thallium (III) acetate and mercuric acetate gave stable phenyl-thallium and phenylmercury salts respectively. However, biphenyl was the product formed from palladium (II) and platinum (II) acetates:



By analogy with the reactions of thallium (III) and mercury (II) salts, Davidson postulated the intermediacy of  $\sigma$ -bonded aryl-palladium (II) and arylplatinum (II) complexes and suggested that the reactions were examples of electrophilic substitution reactions similar to mercuration in which an aromatic hydrogen was replaced by the metal to yield the arylmetal salt. The involvement of phenyl radicals was dismissed by both van Helden<sup>7</sup> and Davidson<sup>9</sup> because the dimerisation was insensitive to radical scavengers.

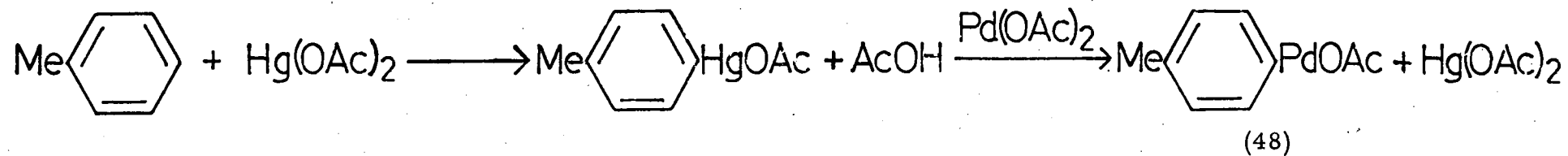
For the reaction between palladium acetate and benzene- $d_6$  Davidson<sup>9</sup> observed a primary kinetic isotope effect ( $k_H/k_D = 5.0$ ) which is similar to the isotope effect observed in electrophilic mercuration:<sup>62</sup>



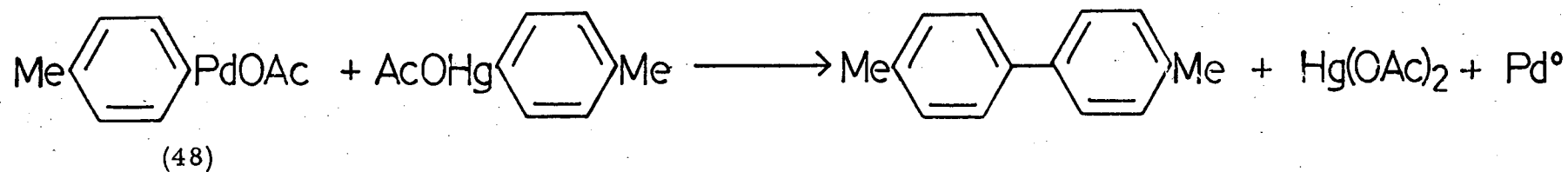
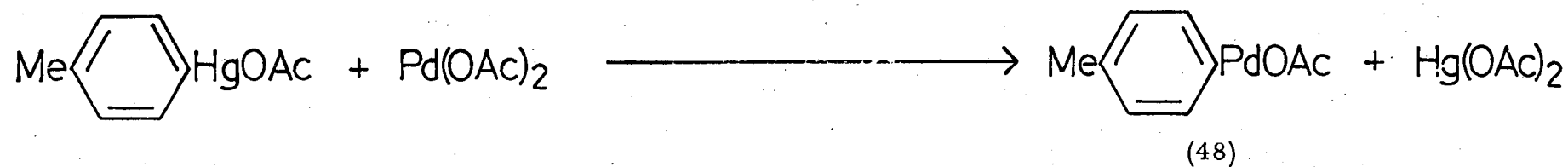
The presence of perchloric acid was found to have a strongly accelerating effect on aryl coupling, an effect which was explained by the increased electrophilicity of palladium (II) caused by perchloric acid.

Unger and Fouty<sup>85</sup> investigated the oxidative coupling of toluene in the presence of mercury (II) and palladium (II) salts. Conversion to bitolyls was in only about 60% yield in the presence of palladium (II) salts. However, addition of mercuric acetate in increasing amounts gave quantitative yields of bitolyl, the yield of the *p, p'*-isomer increasing to about 70% for a mercury to palladium ratio of 2:1. Brown and McGarry<sup>92</sup> had reported that mercuration occurred mainly in the para-position and so Unger and Fouty suggested that mercuration of toluene occurred, again giving mainly the para-isomer, followed by replacement of mercury by palladium





Scheme 18

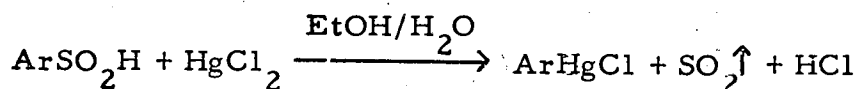


Scheme 19

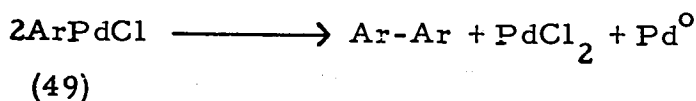
[Scheme 18]. Bitolyl formation was investigated using pre-formed mercuric compounds, *p*-tolylmercuric acetate and bis(*p*-tolyl)mercury (II). Only *p*, *p'*-bitolyl was formed. These workers then suggested that reaction with *p*-tolylmercuric acetate occurred as shown [Scheme 19]. It is proposed that tolylpalladium acetate (48) reacts with tolylmercuric acetate to give the coupled product. Addition of perchloric acid to the reaction mixture caused the rate of aryl coupling to increase and formation of other bitolyl isomers to occur, both of which are possibly due to a more electrophilic arylpalladium complex which is capable of reacting not only with *p*-tolylmercuric acetate but also with the toluene present.

Heck<sup>30</sup> proposed that arylation of alkenes occurred via arylpalladium complexes prepared in situ from the corresponding arylmercuric salt and palladium (II) compounds [Introduction p. 5]

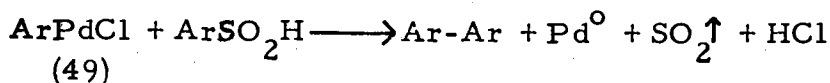
Garves<sup>52</sup> prepared arylpalladium complexes by an identical route to that used in the preparation of arylmercuric salts, that is the desulphination of aromatic sulphinic acids.



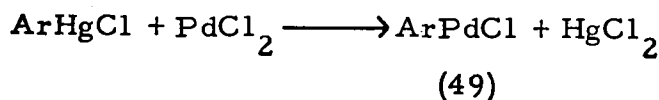
Replacement of mercuric chloride with palladium (II) chloride gave a reaction in which biaryls were formed presumably via decomposition of two arylpalladium species (49). Reaction of the arylpalladium



species with the sulphinic acid is also possible. Addition of mercuric



chloride was found to give increased yields of biaryl which is in agreement with the findings of Unger and Fouty,<sup>85</sup> the reaction now proceeding via reaction of arylmercuric chloride with palladium



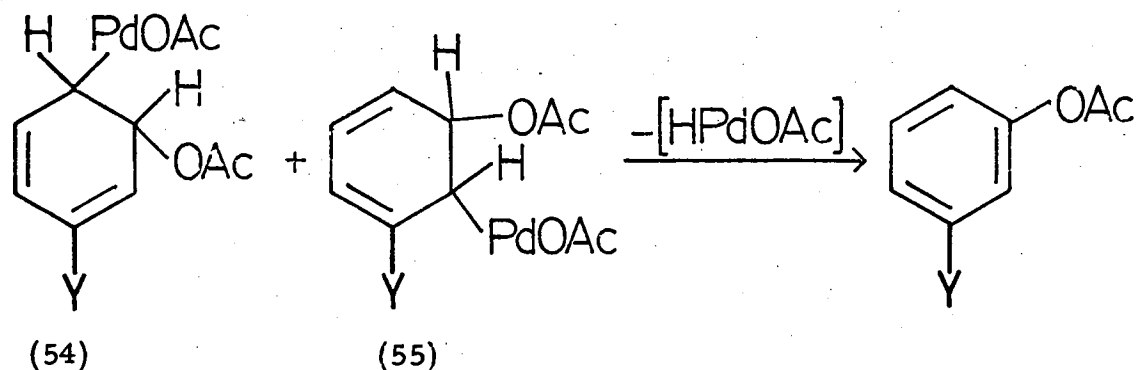
chloride. Biaryl formation could then occur by decomposition of two arylpalladium species or by reaction of the arylmercuric and arylpalladium chlorides [see Scheme 19].

Eberson and Gomez-Gonzalez,<sup>84, 87, 93</sup> investigating the nuclear acetoxylation of aromatic compounds in the presence of palladium acetate under oxygen, found that benzenes containing electron-releasing substituents gave mainly meta-acetoxyated products. Again intermediacy of an arylpalladium complex was invoked.

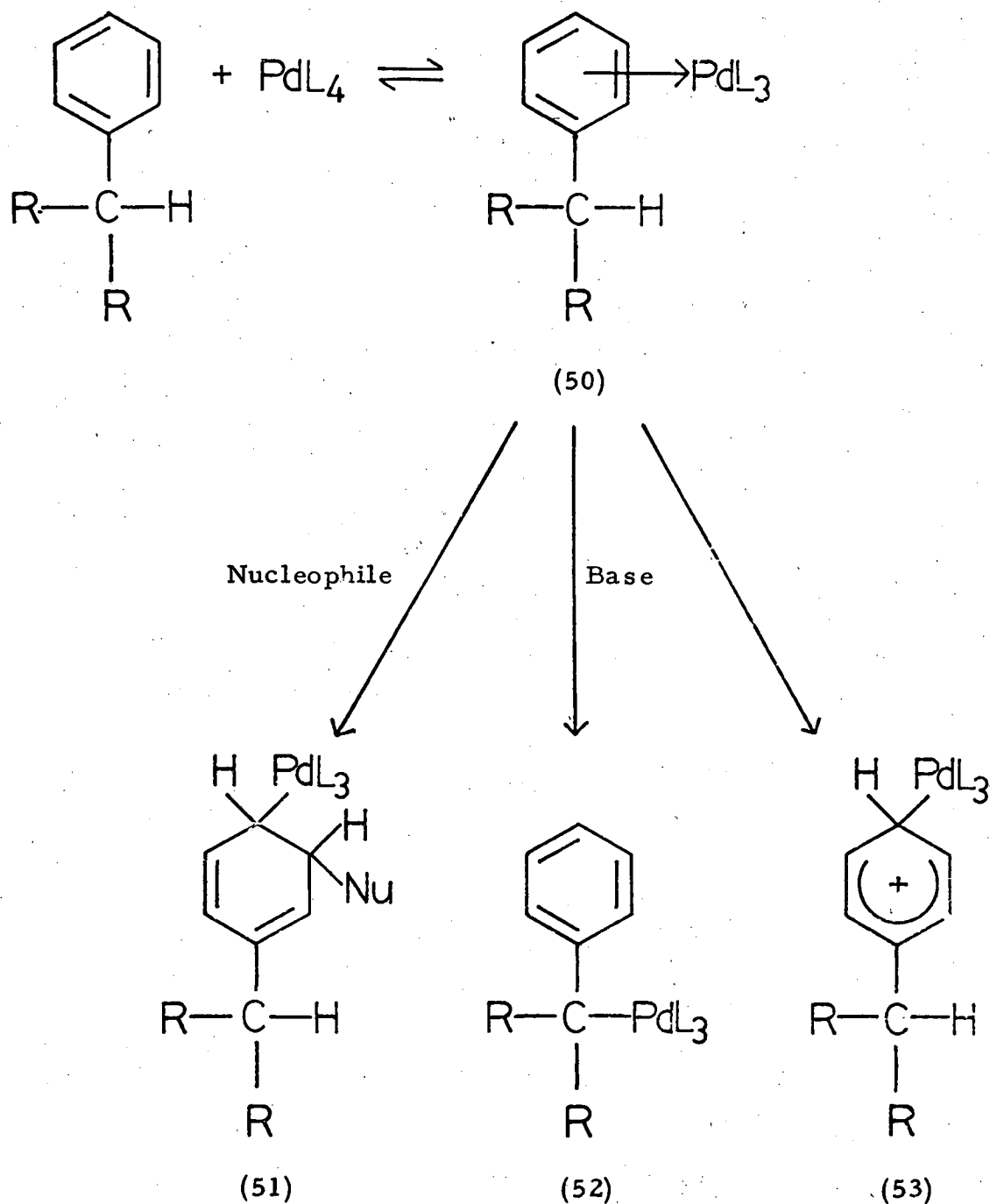
These workers reviewed reactions in which arylpalladium complexes were postulated as intermediates. They then proposed that the initial step in the reaction between aromatic compounds and palladium (II) complexes is formation of a  $\pi$ -complex (50) which can undergo one of three reactions depending on its structure and on the reaction conditions, [Scheme 20]:

- 1) nucleophilic attack at the ring to form an arylpalladium adduct (51),
- 2) attack of base at an  $\alpha$ -hydrogen to form a benzylpalladium substitution intermediate (52),
- 3) collapse to a Wheland-type intermediate (53).

The inverse isomer distribution pattern observed in the nuclear acetoxylation of aromatic compounds is now easily explained. Palladium (II) becomes attached to those ring positions which are susceptible to electrophilic attack giving species (54) and (55), of the same form as (51). Subsequent loss of hydridopalladium acetate affords the meta-isomer, as illustrated.

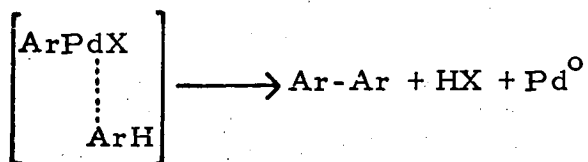


Y:- t-butyl, MeO and Cl



Scheme 20

Eberson and Gomez-Gonzalez<sup>87</sup> proposed that biaryl formation occurs via a Wheland-type intermediate of the same form as (53) and tentatively postulated the following step in which reaction occurs via coordination of further aromatic compound to the palladium of the arylpalladium species:

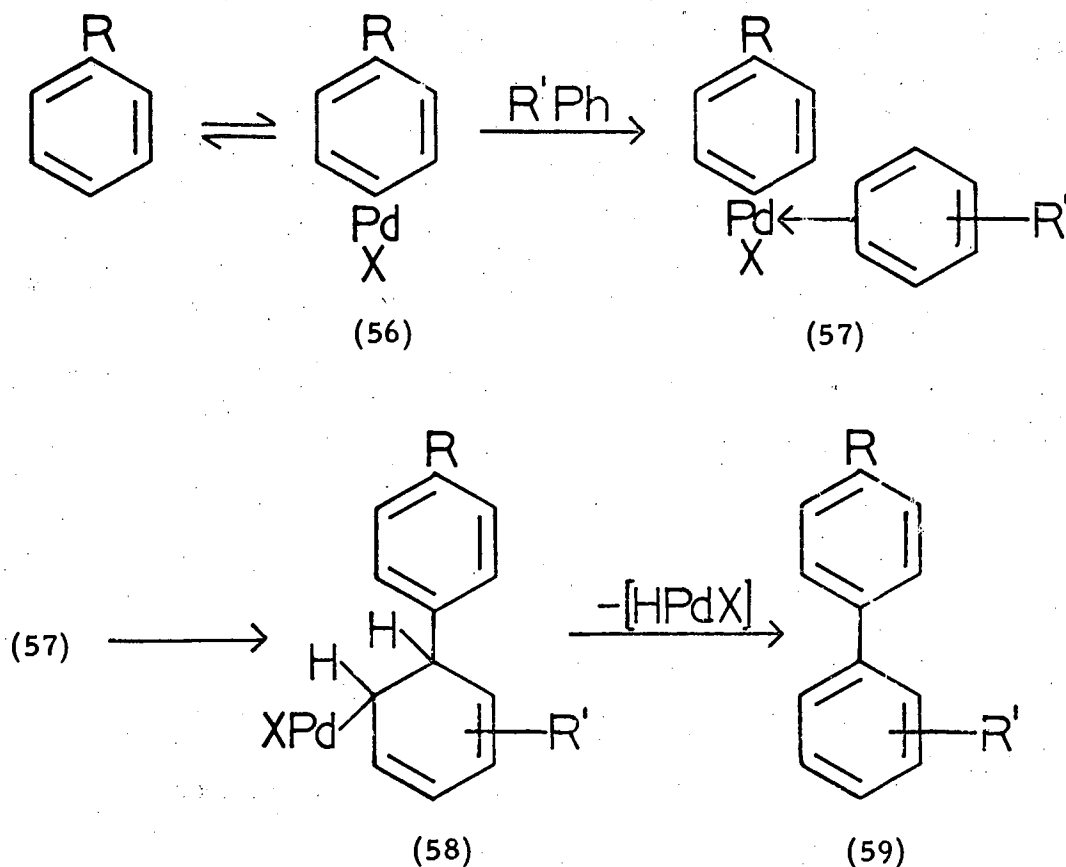


Norman *et al.*<sup>59</sup> studied palladium (II)-assisted oxidative coupling of benzenes in trifluoroacetic acid. Most of the possible isomers were found, but the predominant ones were those in which one of the aryl groups is bonded to the second through the position most susceptible to electrophilic attack. For example, from the coupling of nitrobenzene about 80% of the dinitrophenyls is accounted for by isomers substituted at the 3-position in at least one ring but only about 20% is the 3, 3'-isomer.

It was also found that in the reaction between benzene and nitrobenzene there was little selectivity in the formation of the three nitrobiphenyls but that in the formation of methoxybiphenyls from benzene and anisole there was significant selectivity.

Norman's rationale is that one of the two aromatic nuclei reacts preferentially at the position(s) which is the most susceptible to electrophilic attack, whereas the other nucleus reacts in a less discriminatory fashion. In the formation of nitrobiphenyls, benzene would be the more discriminating component whereas in methoxybiphenyl formation anisole would be the discriminating component. The mechanism proposed is shown in Scheme 21. Reaction of the aromatic compound with the palladium compounds affords the arylpalladium species (56) which reacts with another substituted benzene to give a  $\pi$ -complex (57). Insertion of the  $\pi$ -bonded arene into the aryl-carbon to palladium  $\sigma$ -bond gives adduct (58), similar to the adduct (6) proposed by Heck [Scheme 14] for the insertion of an alkene into an aryl-carbon to palladium  $\sigma$ -bond, and loss of a hydridopalladium species from (58) yields the biphenyl. It is thought that the greater selectivity occurs in the first step, [formation of intermediate (56)].

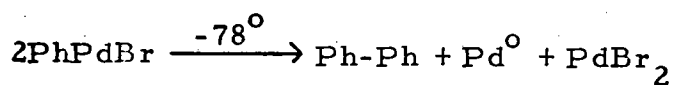
In none of the reactions discussed has the intermediacy of an arylpalladium species been proved but its existence is consistent



Scheme 21

with much experimental data. Its formation is considered to occur via an electrophilic aromatic substitution akin to formation of arylmercuric salts. Such a palladium complex would probably be stabilised by ligands present in the reaction mixture.

Very recently, however, Klabunde<sup>94</sup> reported the formation of several arylpalladium halides by the oxidative insertion of palladium atoms into aryl-carbon to halogen bonds at low temperatures. These species, with no other ligands present, decompose to biaryls as shown.

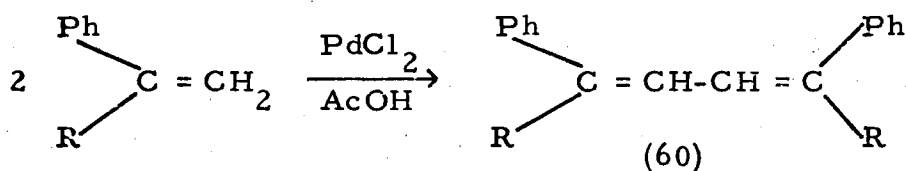


This report when taken along with the circumstantial evidence from the reactions discussed makes the existence of arylpalladium complexes very likely.

## 2.2 Evidence for the Existence of Alkenylpalladium Complexes

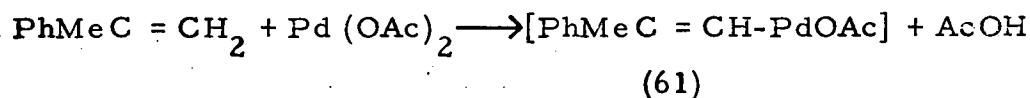
$\sigma$ -Alkenylpalladium complexes are known, having been prepared from an alkene and a triphenylphosphinepalladium (0) complex by Fitton and McKeon.<sup>95</sup> There is also evidence for their intermediacy in reactions, especially in the oxidative coupling of alkenes.

Oxidative coupling of alkenes was first reported by Hüttel *et al.*<sup>96, 97</sup> who obtained 1,4-diphenylbuta-1,3-dienes (60) from the coupling of  $\alpha$ -substituted styrenes by palladium chloride in acetic acid.



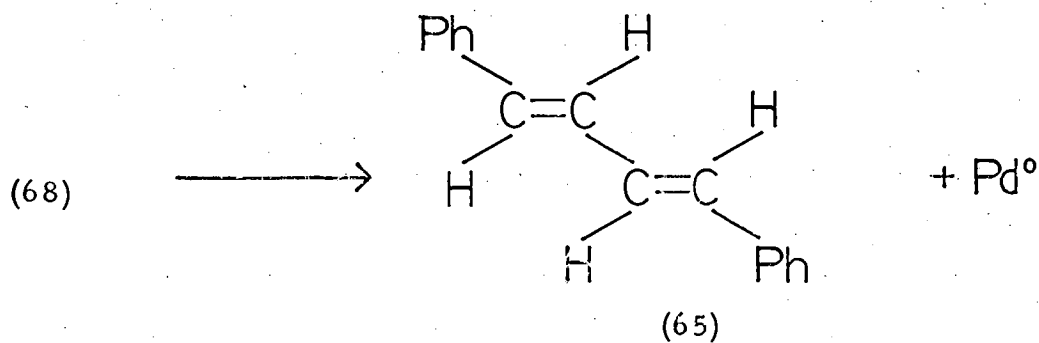
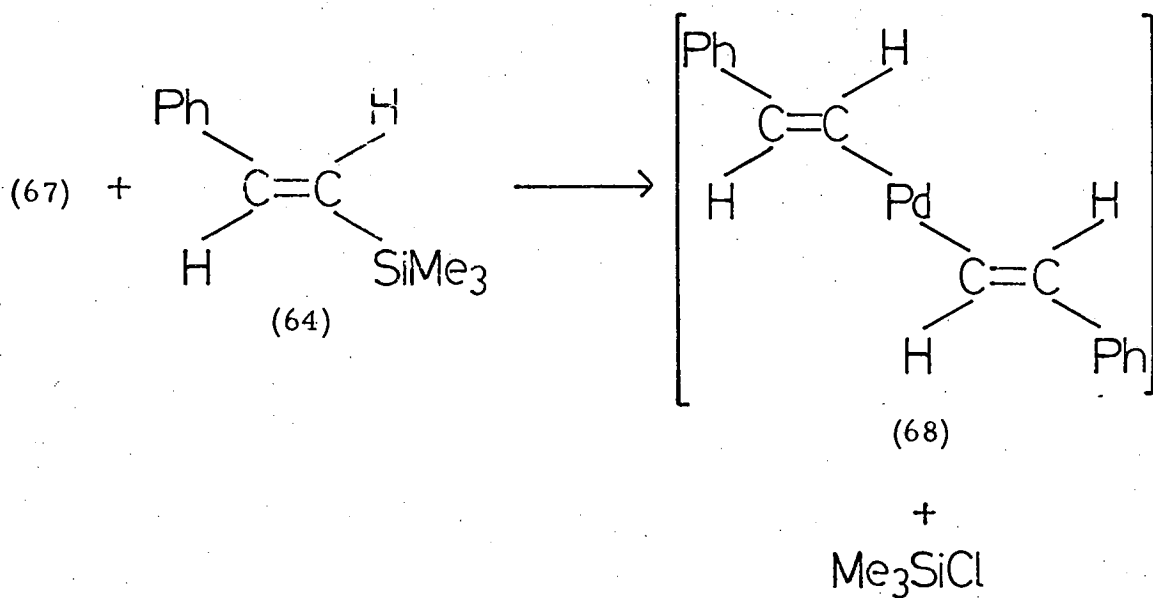
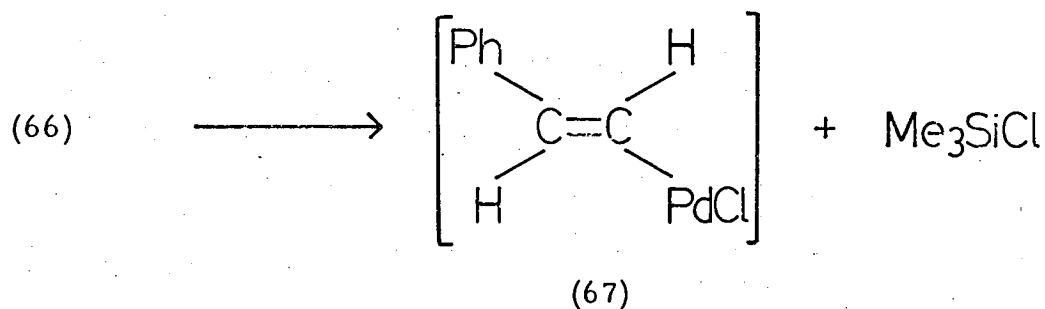
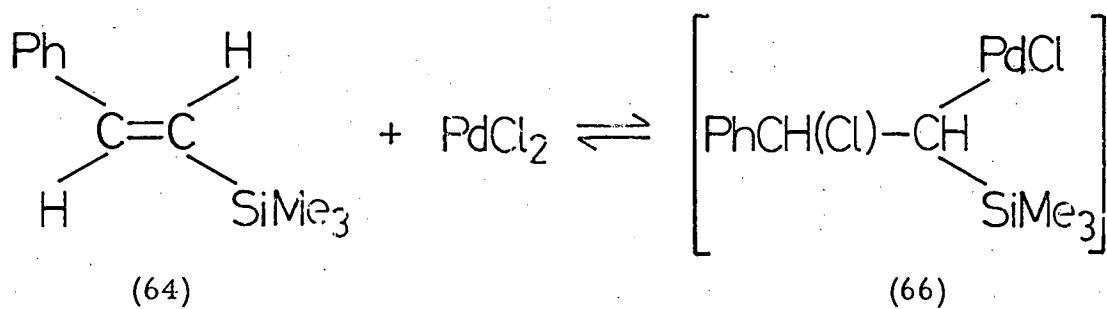
R:- Me, Ph

When Volger<sup>49, 98, 99</sup> investigated this coupling reaction with palladium acetate and sodium acetate in acetic acid, a bimolecular  $\pi$ -complex was suggested as an intermediate. Maitlis,<sup>100</sup> however, proposed formation of a  $\sigma$ -vinylpalladium acetate (61).



Reaction of the alkene complex (61) with more substituted styrene by cis-addition through (62) gives the addition complex (63) from which elimination of hydridopalladium acetate affords the coupled alkene [Scheme 22].

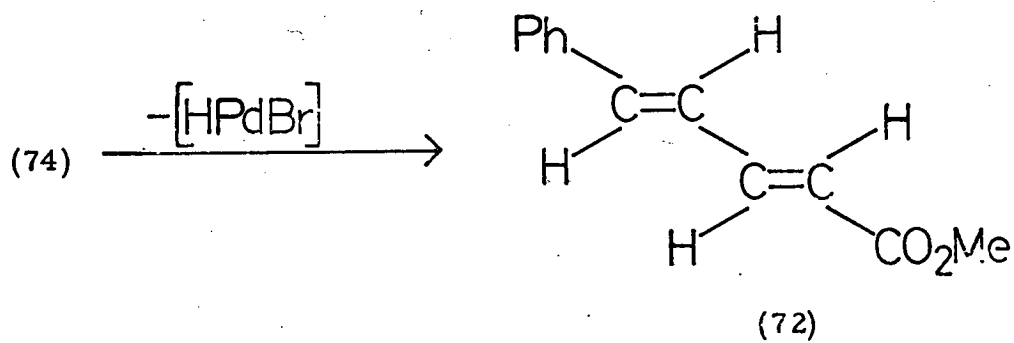
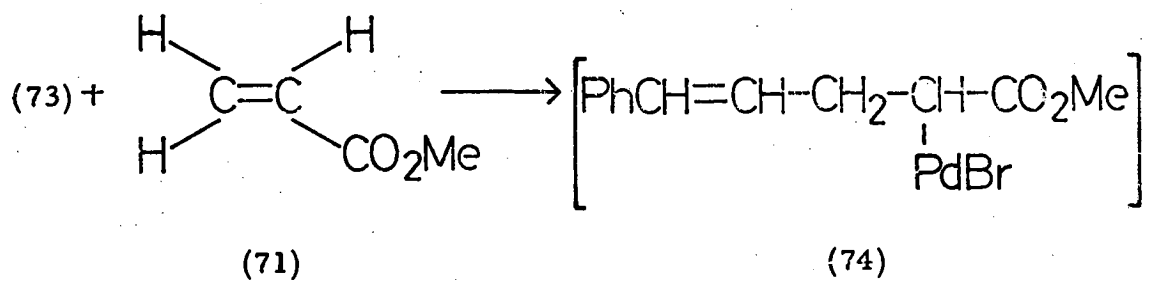
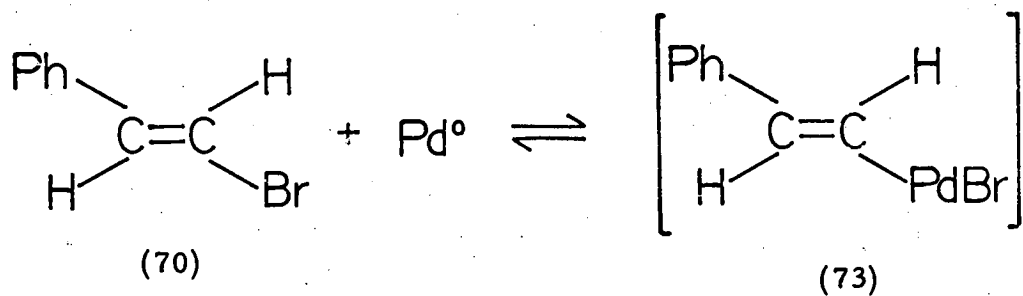
In 1971, Weber and co-workers<sup>101</sup> published the findings of their investigations into the reactions of vinylsilanes with palladium salts. The reaction of  $\beta$ -trimethylsilylstyrene (64)



Scheme 23

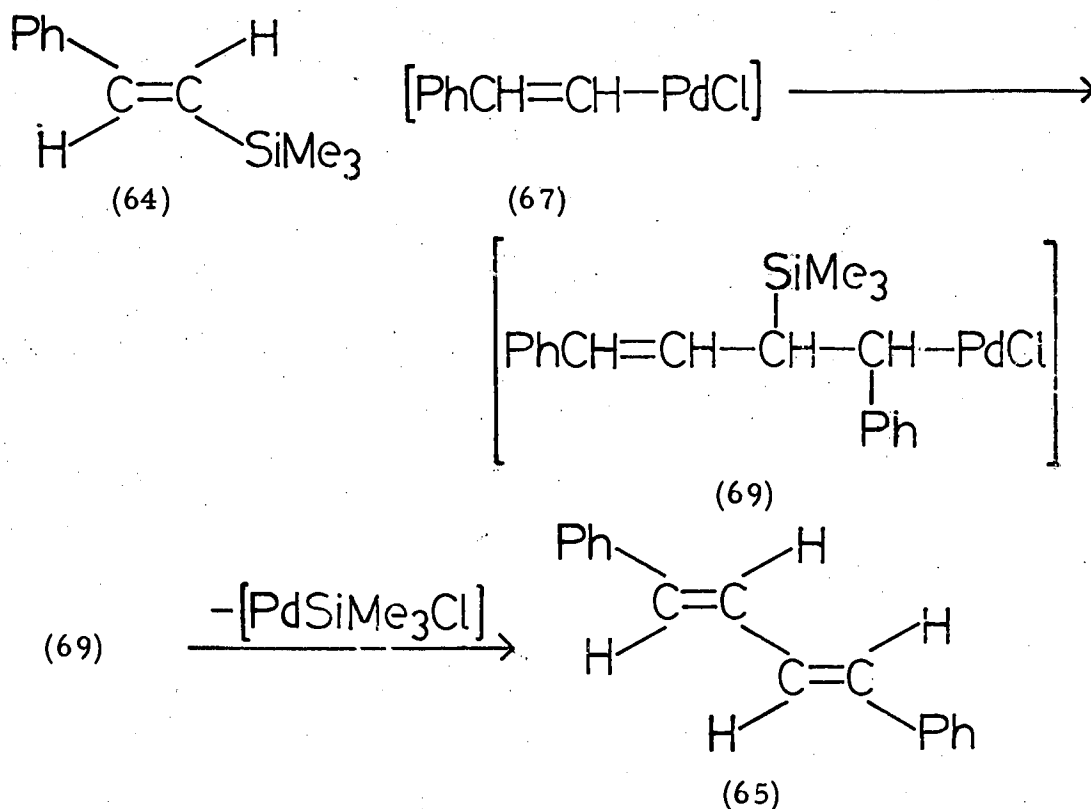






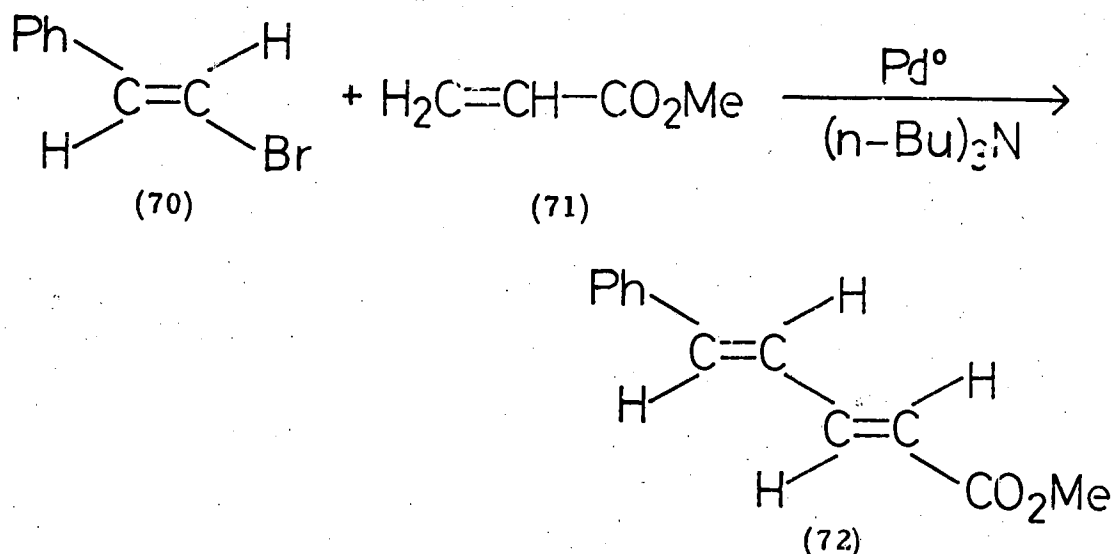
Scheme 25

alkene-palladium complex (67) would give complex (69) decomposition of which would afford the product (65), [Scheme 24].



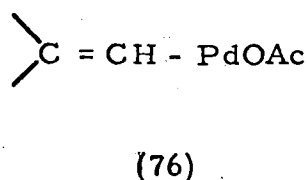
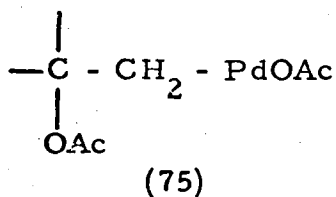
Scheme 24

In 1972, Heck<sup>37</sup> reported that olefinic compounds react with aryl, benzyl and styryl halides in the presence of a catalytic amount of palladium metal (prepared in situ) and a hindered amine to form vinylic compounds in which the aryl, benzyl or styryl group has replaced a vinylic hydrogen of the original alkene. This reaction is illustrated by the reaction of trans- $\beta$ -bromostyrene (70) and methyl acrylate (71) to yield the substituted butadiene (72). Heck presumes that the organic halide and palladium metal form a very reactive solvated organopalladium (II) halide (73). The reaction with trans- $\beta$ -bromostyrene (70) could then occur as shown, [Scheme 25]. The organopalladium halide (73) then reacts with methyl acrylate (71) by cis-addition of (73) across the olefinic double bond of the alkene (71) to give adduct (74). cis-Elimination of hydridopalladium bromide from adduct (74) affords the butadiene (72).

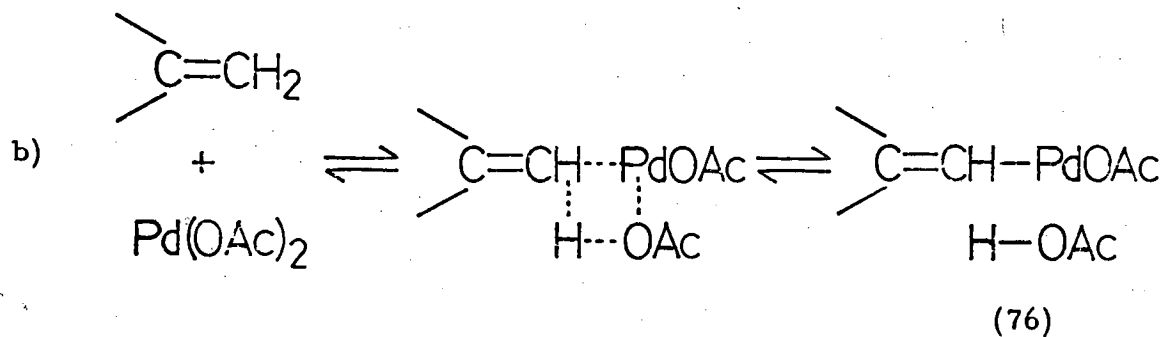
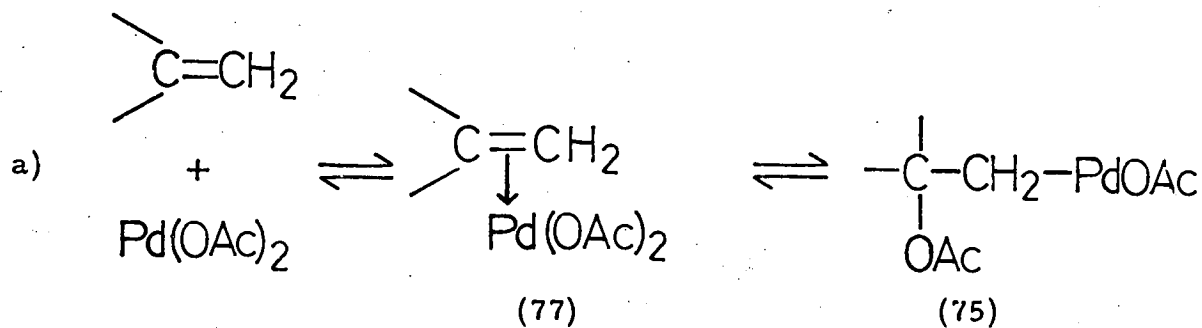


Recently Kikukawa et al.<sup>102</sup> studied the oxidation of isobutene and methylcycloalkenes by palladium acetate. Two types of oxidation were identified after reaction of the alkene and palladium acetate in acetic acid at between 30° and 80° for between 10 h and 40 h: acetoxylation to allylic acetates and oxidative coupling to give dimeric alkenes. Reactions of the same alkenes were carried out under carbon monoxide, which is known to insert into carbon-palladium  $\sigma$ -bonds,<sup>103</sup> the products being allylic acetates and unsaturated esters.

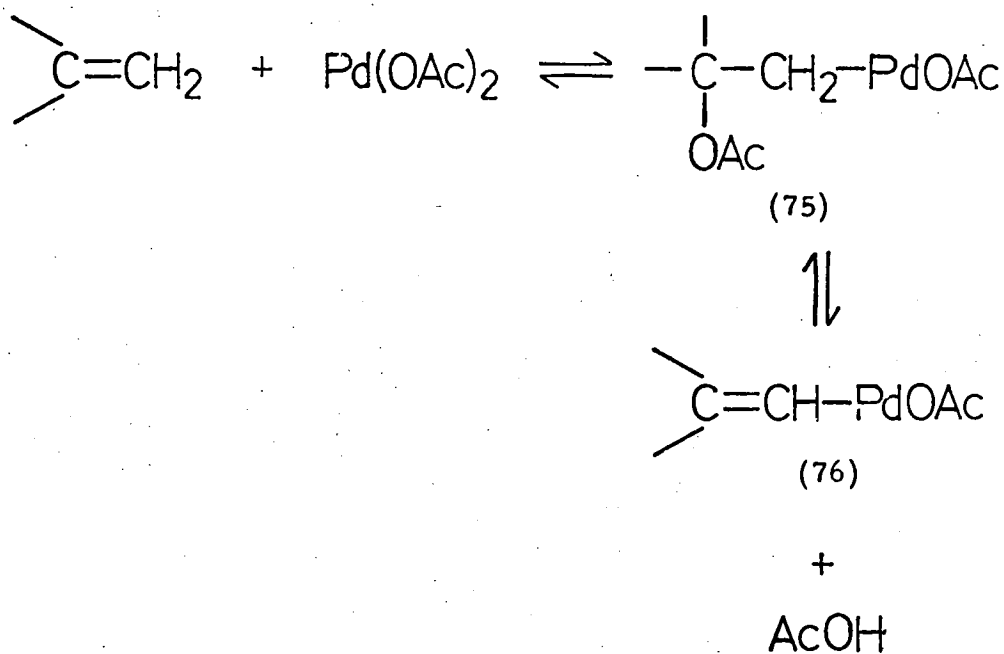
Kikukawa attempted to detect, by a method unreported, a palladium intermediate in the reaction between alkene and palladium acetate in acetic acid. Since none was detected it was suggested that the species responsible for insertion of carbon monoxide, and probably for alkene insertion, is in rapid equilibrium with the alkene and palladium acetate. Two species (75) and (76) seemed attractive and were considered.



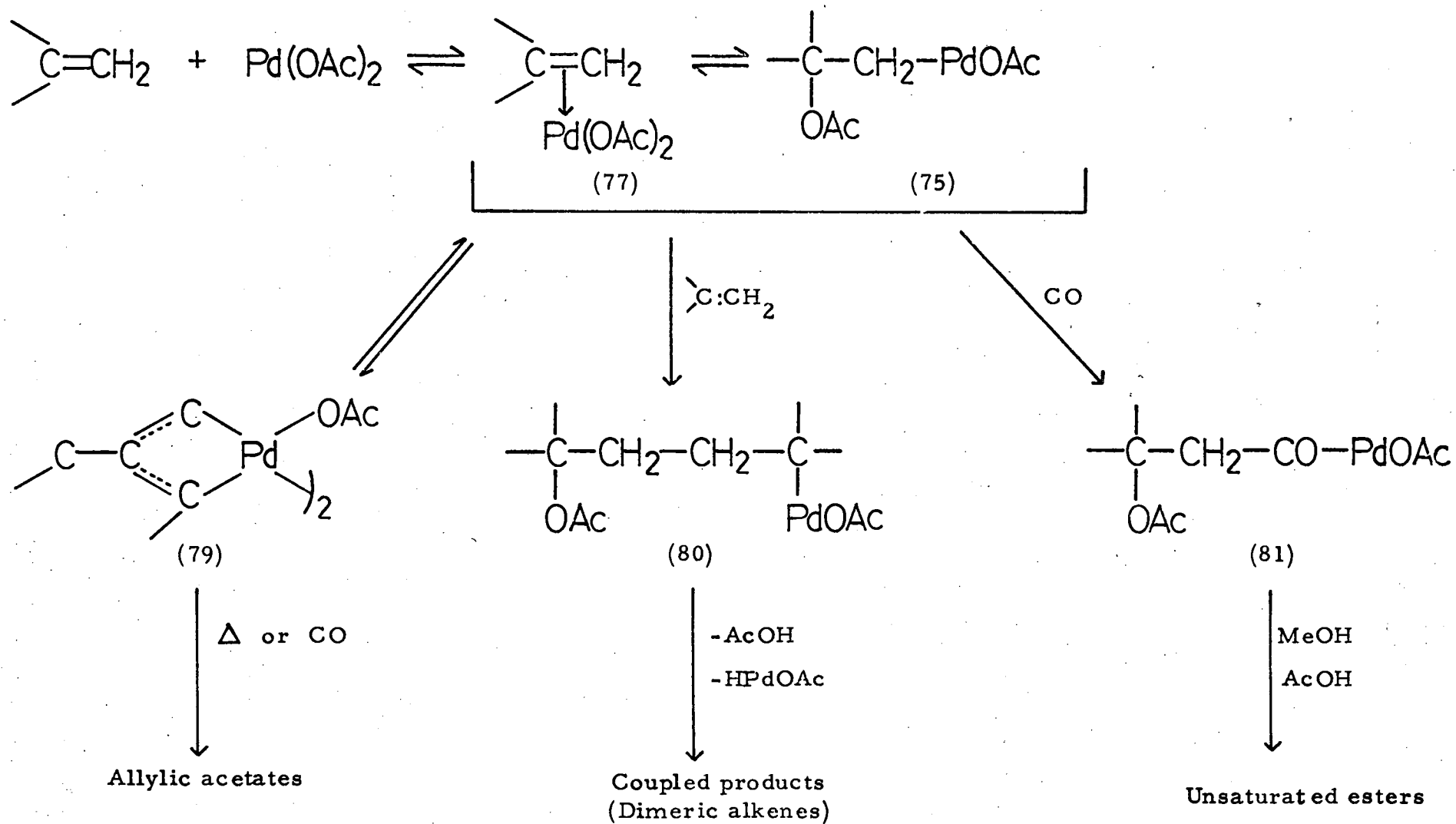
The alkenyl complex (76) was considered inadequate to



Scheme 26



Scheme 27

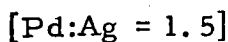
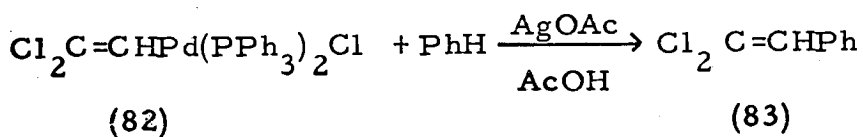


Scheme 28

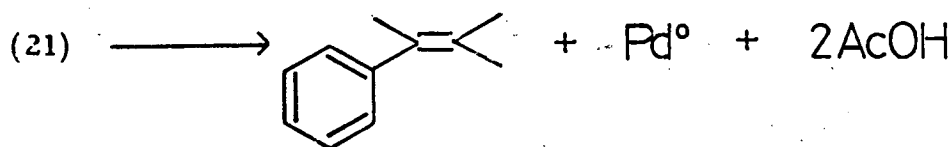
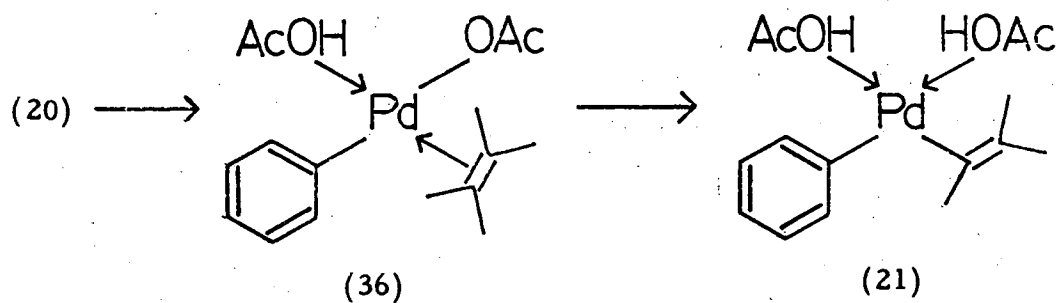
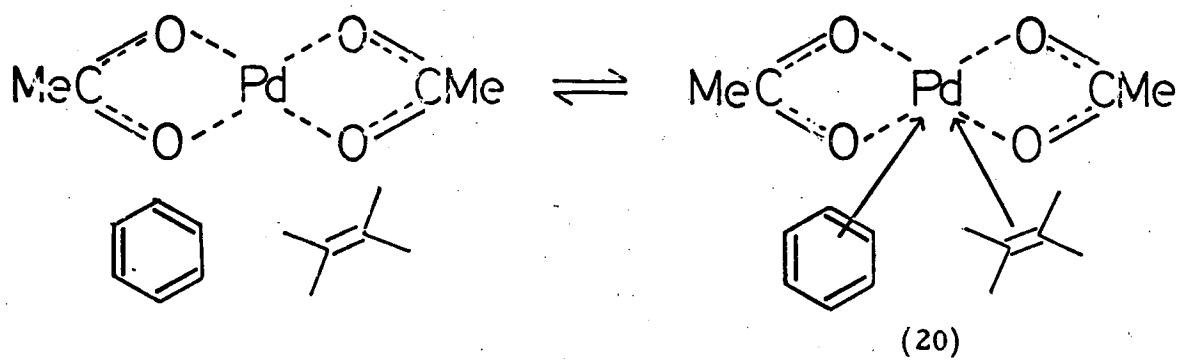
account for the fast equilibrium between alkene and palladium acetate and so adduct (75) was proposed as the reaction intermediate. Fast equilibrium between adduct (75) and free alkene would occur through the  $\pi$ -alkene complex (77) as shown, [Scheme 26a]. It is feasible, however, that the alkenyl complex (76) could be in fast equilibrium with free alkene because, in acetic acid, the equilibrium can be envisaged as proceeding through the four-centre intermediate (78), [Scheme 26b]. It is also possible that the alkenyl complex (76) could decompose to alkene and palladium acetate through the acetoxyadduct (75), [Scheme 27].

A reaction mechanism for the oxidation of alkenes was proposed proceeding through either the  $\pi$ -alkene complex (77) or the acetoxy adduct (75) as illustrated in Scheme 28. Allylic acetates were formed by reaction through complex (79). Formation of  $\pi$ -allylic-palladium complexes similar to (79) is well known.<sup>6e</sup> Reaction of alkenes or carbon monoxide with the reactive palladium intermediate [either (77) or (75)] occurs by insertion of the alkene or carbon monoxide respectively to give the corresponding adducts, (80) and (81), decomposition of which affords the products.

In 1970, Moritani and co-workers<sup>26, 27</sup> reported the arylation of  $\sigma$ -vinylpalladium complexes by an aromatic compound in the presence of silver acetate. Thus reaction of chloro- $\sigma$ -( $\beta$ ,  $\beta$ -dichlorovinyl)-trans-bis(triphenyl phosphine) palladium (II), (82) with benzene in the presence of silver acetate and acetic acid produced  $\beta$ ,  $\beta$ -dichlorostyrene (83) in 80% yield.

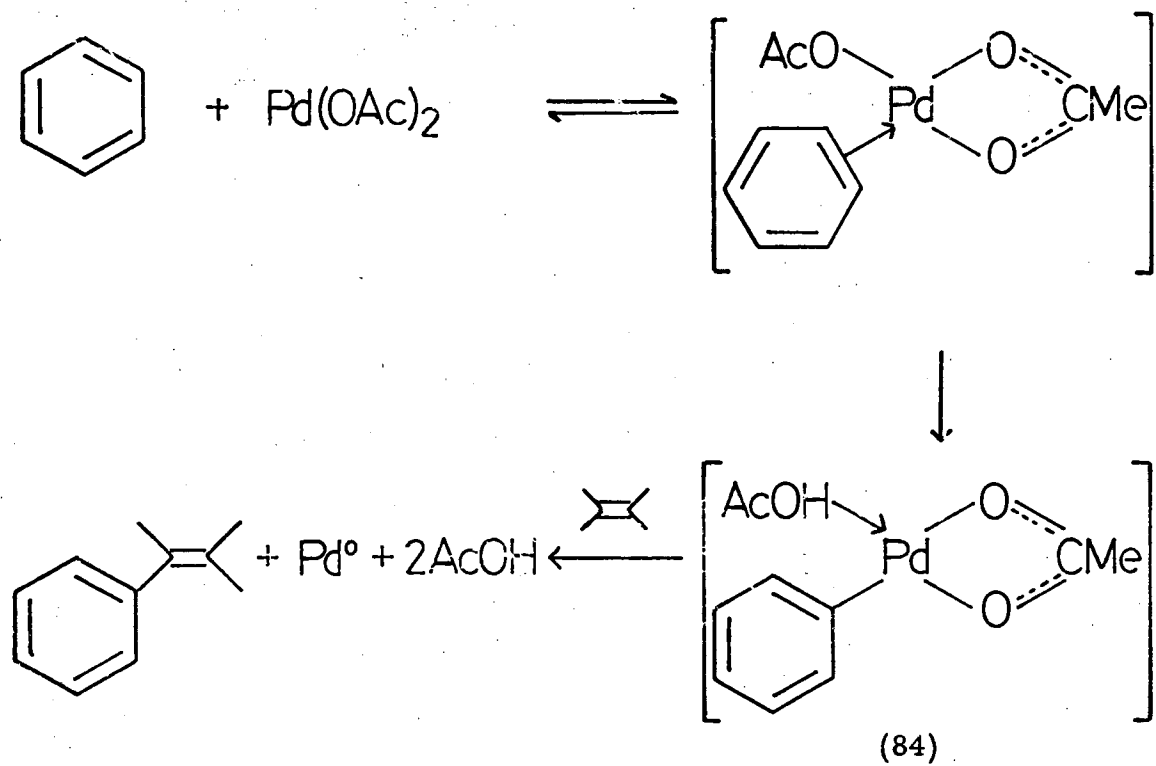


This reaction is good evidence that alkene arylation can occur through  $\sigma$ -alkenylpalladium complexes but this does not necessarily mean that alkene arylation proceeds by this route under the reaction conditions used in the current work.

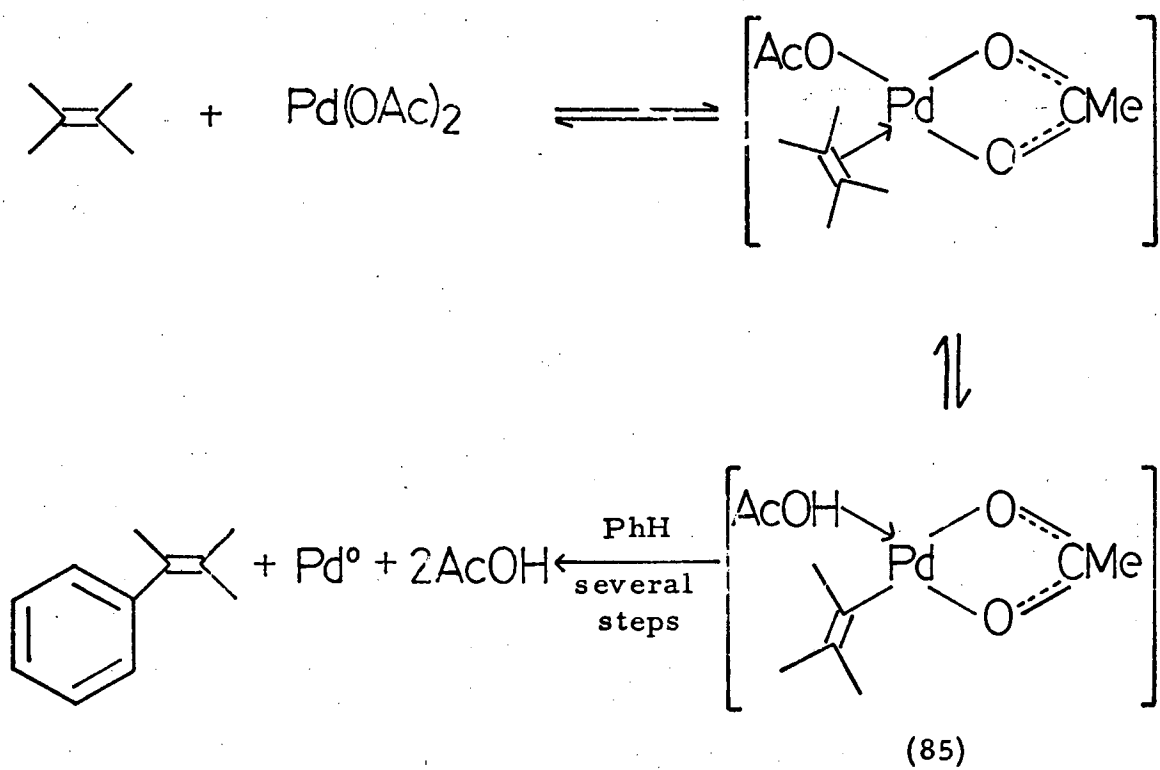


Scheme 10





Scheme 29



Scheme 30

### 2.3 Possible Mechanisms for the Palladium(II)-Assisted Arylation of Alkenes

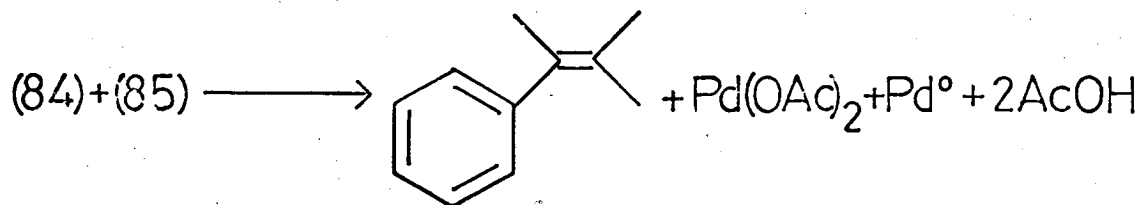
Discussion Sections 2.1 and 2.2 (p. 78 ) have demonstrated that the intermediacy of both  $\sigma$ -arylpalladium complexes and  $\sigma$ -alkenylpalladium complexes in palladium-assisted reactions of alkenes is probable and so their involvement in palladium(II)-assisted arylation of alkenes is also feasible. The reaction pathways suggested in Scheme 15 are expanded below and results from this investigation and from previous work will be discussed in relation to these expanded pathways.

(1) A mechanism identical to that proposed by Moritani except that the rate-determining step is that which involves  $\sigma$ -bond formation between palladium and the aromatic compound (Scheme 10). It should also be noted that reaction of the double  $\pi$ -complex (20) could occur via a  $\pi$ -aryl- $\sigma$ -alkenylpalladium species to give the double  $\sigma$ -complex (21) instead of reaction via the  $\pi$ -alkene- $\sigma$ -aryl species (36) to give complex (21).

(2) The mechanism proposed by Heck<sup>39, 40</sup> and by Boyd<sup>48</sup> (Scheme 29). Once again, aryl-palladium  $\sigma$ -bond formation is postulated as the rate-determining step. The structure of the  $\sigma$ -arylpalladium complex (84) is not yet known.

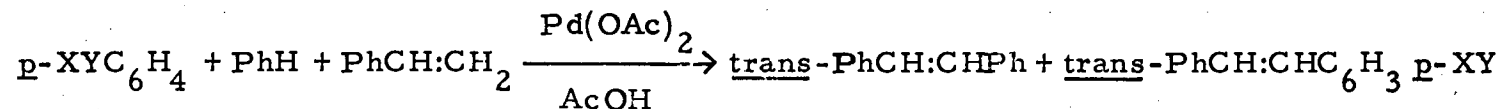
(3) A mechanism involving  $\sigma$ -alkene-palladium complex formation (85), followed by rate-determining reaction with the benzene (Scheme 30).

(4) A mechanism involving reaction of the  $\sigma$ -arylpalladium species (84) and the  $\sigma$ -alkenyl species (85).



Here it is assumed that species (84) and (85) are formed as

Table 30 Competitive Arylation of Styrene. Palladium Acetate (Batches 10 and 11)



X	Y	Pd(OAc) <sub>2</sub> Batch	Product Isomer Distribution (%)			Stilbene (%)	Substituted Stilbene (%)	Partial Rate Factors			Reactivity Ratio ( <sup>k</sup> <sub>X</sub> / <sup>k<sub>H</sub>)</sup>
			<u>o</u>	<u>m</u>	<u>p</u>			<u>f</u> <sub>o</sub>	<u>f</u> <sub>m</sub>	<u>f</u> <sub>p</sub>	
Me	H	10	27.6	72.6*		15.3	23.2	1.26	≤3.31	≤6.62	1.52 <sup>†</sup>
Me	H	11	27.5	72.5*		15.1	22.7	1.24	≤3.26	≤6.52	1.50 <sup>†</sup>
Me	Me	11	←100→			12.7	15.7	←1.85→			1.23 <sup>††</sup>
Me	Me	11	←100→			9.2	13.1	←2.15→			1.43
OMe	H	10	33.0	5.2	61.8	6.9	40.1	5.79	0.92	21.68	5.85 <sup>†</sup>
OMe	H	11	33.0	5.0	61.9	7.0	39.5	5.61	0.86	21.03	5.66 <sup>†</sup>
CF <sub>3</sub>	H	10	←100→			13.8	2.0	≤0.42	≤0.42	≤0.84	0.14
CF <sub>3</sub>	H	11	←100→			14.2	2.0	≤0.42	≤0.42	≤0.84	0.14
Cl	H	10	31.1	68.9*		21.4	13.6	0.59	≤1.32	≤2.65	0.64
Cl	H	11	30.4	69.6*		13.8	8.3	0.55	≤1.25	≤2.51	0.60

\* Total meta-plus-para isomers.

<sup>†</sup> Reaction time 20 min.

<sup>††</sup> Reaction time 45 min.

All other reaction times 30 min.

illustrated in Schemes 29 and 30 respectively.

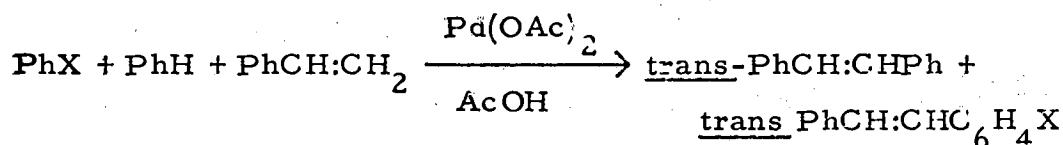
Again, it must be realised that proposals (1)-(4) are only guides to the mechanism on which to base discussion of results.

#### 2.4 Evidence from Competitive Arylations of Styrene

After competitive reactions of styrene with benzene and substituted benzenes (each benzene in 50-fold excess relative to styrene and palladium acetate, batches 10 and 11) were carried out, the percentage yields of substituted and unsubstituted stilbenes and the isomer distributions of the substituted stilbenes were determined. The reactivity ratio ( $k_X/k_H$ ) of substituted benzene to benzene and the partial rate factors of the substituted benzene were calculated. Table 30 lists the results obtained. Because of the difficulty of separation of the isomeric stilbenes by g.l.c. (only with anisole were the three isomers separated) it is not possible to deduce from the product isomer distribution whether electrophilic or nucleophilic aromatic substitution occurs. Certainly, the product distribution obtained from anisole is indicative of electrophilic substitution, an electron-donating group causing substitution predominantly at the ortho- and para-positions. The reactivity ratios, however, are a better guide. Aromatic compounds, p-xylene, toluene and anisole, each with at least one electron-donating substituent, give yields of substituted stilbene greater than those of stilbene from benzene. Both trifluoromethylbenzene and chlorobenzene, each with an electron-withdrawing substituent, are less reactive than benzene. These results suggest that electrophilic aromatic substitution, rather than nucleophilic substitution, occurs.

It is of interest to compare the results obtained by Moritani<sup>17, 61</sup> and by Boyd<sup>48</sup> from the competitive arylation of styrene with those obtained from the current work (Table 30). The data are recorded in Table 31. The original results published by Moritani<sup>17</sup> (Table 31: C) are at variance with those found in the

**Table 31**    Comparison of Results Obtained from Competitive Arylations of Styrene



X	Product Isomer Distribution			Partial Rate Factors			Reactivity Ratio ( $k_X/k_H$ )
	<u>o</u>	<u>m</u>	<u>p</u>	$f_o$	$f_m$	$f_p$	
Me	A	27.6	72.6*	1.26	≤3.31	≤6.62	1.52
	B	27.9	72.1*	1.34	≤3.45	≤6.91	1.60
	C	3.8	0	0.08	0	4.17	0.72
	D	24.3	31.5	44.2	1.56	2.02	5.68
OMe	A	33.0	5.2	61.8	5.79	0.92	21.68
	B	35.8	5.8	58.5	2.75	0.44	9.00
	D	36.5	5.4	58.2	5.65	0.83	18.04
CF <sub>3</sub>	A	←—— 100 ———→		≤0.42	≤0.42	≤0.84	0.14
	B	1.4	80.4	18.2	0.008	0.44	0.20
Cl	A	31.1	68.9*	0.59	≤1.32	≤2.65	0.64
	C	5	25	70	0.09	0.44	2.47
	D	13.8	35.6	50.6	0.29	0.75	2.13
NO <sub>2</sub>	B	14.9	77.7	7.4	0.04	0.22	0.04
	C	0	100	0	0	1.50	0
	D	7.7	83.9	8.4	0.06	0.65	0.13

A:- Current work: Palladium acetate batch 10. See Table 30 for reaction conditions.

B:- Boyd<sup>48</sup>: Various reaction temperatures between 93° and 100° for 8 h.

C:- Moritani<sup>17</sup>: Reaction temperature 90° for 8 h.

D:- Moritani<sup>61</sup>: Reaction conditions unknown.

\*:- Total meta-plus para-isomers.

†:- Product isomer distributions and reactivity ratios were not published but were calculated from the partial rate factors.

present work (Table 31: A), by Boyd<sup>48</sup> (Table 31: B) and by Moritani himself<sup>61</sup> (Table 31: D). Moritani's original results show aromatic compounds with either electron-withdrawing or electron-releasing groups to be less reactive than benzene whereas the other three sets of results in Table 31 show that benzenes with electron-releasing substituents are more reactive, and that benzenes with electron-withdrawing substituents are less reactive, than benzene. The variations found by the various workers in the reactivity of each substituted benzene, except Moritani's original results (Table 31: C), can be explained by an argument analogous to that applied to the arylation of styrene with *p*-xylene. For convenience the reasoning is reproduced.

Consider a situation in which a substituted benzene reacts with styrene more quickly than does benzene. Substituted stilbene, therefore, appears more quickly than stilbene. Both stilbene and substituted stilbene can react either with benzene or substituted benzene and, if it is assumed that further phenylation or arylation of the stilbenes is equally facile, then further reaction of the substituted stilbene will occur more quickly than that of stilbene. If the reaction is analysed only for stilbene and substituted stilbene then the reduction in the yield of substituted stilbene due to further reaction will be greater than the reduction in the yield of stilbene due to further reaction and so the substituted benzene will appear to be less reactive than it actually is. Also the further along the reaction coordinate the greater will be the discrepancy between the apparent and actual reactivity of the substituted benzene.

A similar situation would arise in a competitive arylation in which the substituted benzene reacted more slowly than benzene. In this case, the apparent reactivity of the substituted benzene would be too large.

Since, in the current work, competitive arylations were normally carried out for 30 minutes or less, the yields of diarylated products are small and the results obtained herein are thought to be

more accurate than those previously reported by Boyd<sup>48</sup> and Moritani.<sup>17, 61</sup>

If then the results obtained by Boyd,<sup>48</sup> by Moritani<sup>61</sup> and from the current study are considered it is seen that the partial rate factors and reactivity ratios observed in the competitive arylation of styrene cover only a small range. Reactivity ratios vary by a factor of ca. 62 and partial rate factors by a factor of ca.  $2.7 \times 10^3$ . These variations for palladium (II)-assisted arylation of alkenes are less than that usually observed for an electrophilic substitution reaction and it is interesting to compare these results with those from other electrophilic substitutions in the same substituted benzenes as listed in Table 32.<sup>62</sup>

Table 32    Partial Rate Factors and Reactivity Ratios for  
Electrophilic Substitution of Substituted Benzenes.<sup>62</sup>

$$\text{C}_6\text{H}_5\text{X} + \text{Y} \longrightarrow \text{C}_6\text{H}_4\text{XY}$$

X \ Y	NO <sub>2</sub>				Br			
	f <sub>o</sub>	f <sub>m</sub>	f <sub>p</sub>	k <sub>X</sub> /k <sub>H</sub>	f <sub>o</sub>	f <sub>m</sub>	f <sub>p</sub>	k <sub>X</sub> /k <sub>H</sub>
Me	42.4	1.9	62.6	25.2	600	5.5	2420	605
OMe					$8.6 \times 10^7$	-	$1.1 \times 10^{10}$	<u>ca.</u> $2 \times 10^9$
Cl	0.03	0.001	0.137	0.033				
NO <sub>2</sub>				<u>ca.</u> $10^{-5}$				

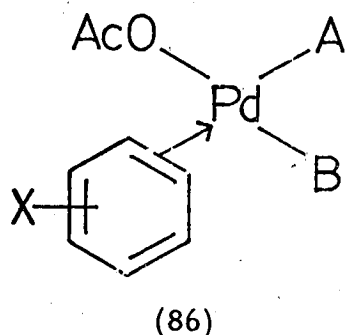
Table 32 illustrates the variation in partial rate factors and reactivity ratios in the electrophilic substitution of substituted benzenes, the partial rate factors varying by a factor of ca.  $10^9$  and the reactivity ratios by a factor of ca.  $10^6$ .

Shue<sup>42</sup> performed the competitive arylation of styrene with benzene and hexadeuterobenzene in the presence of palladium acetate and observed a primary kinetic isotope effect  $k_{\text{H}}/k_{\text{D}} = 5.3$ .

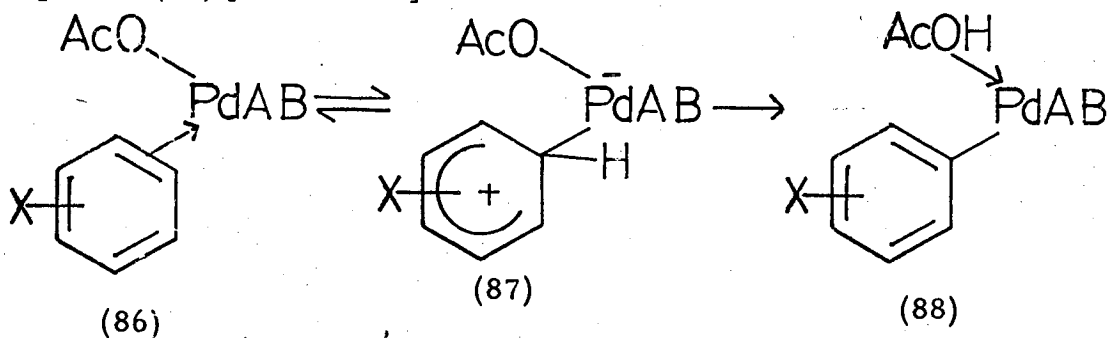
He found no evidence for isotopic scrambling, only benzene- $d_0$  and benzene- $d_6$  being present at the end of the reaction and also no kinetic isotope effect was observed in the reaction between benzene and  $\beta, \beta$ -dideuterostyrene. These results suggest that it is irreversible cleavage of a hydrogen to aromatic carbon bond which is rate-determining.

The mechanism of palladium (II) assisted arylation of styrene must be capable of explaining the evidence obtained so far, that is, that electrophilic substitution of the aromatic compound is possible and gives a narrow range of effects.

All four mechanisms discussed previously (Discussion p. 92) can explain the occurrence of electrophilic aromatic substitution. Coordination of the benzene to palladium gives, in each mechanism, a  $\pi$ -arene palladium complex of the type (86).

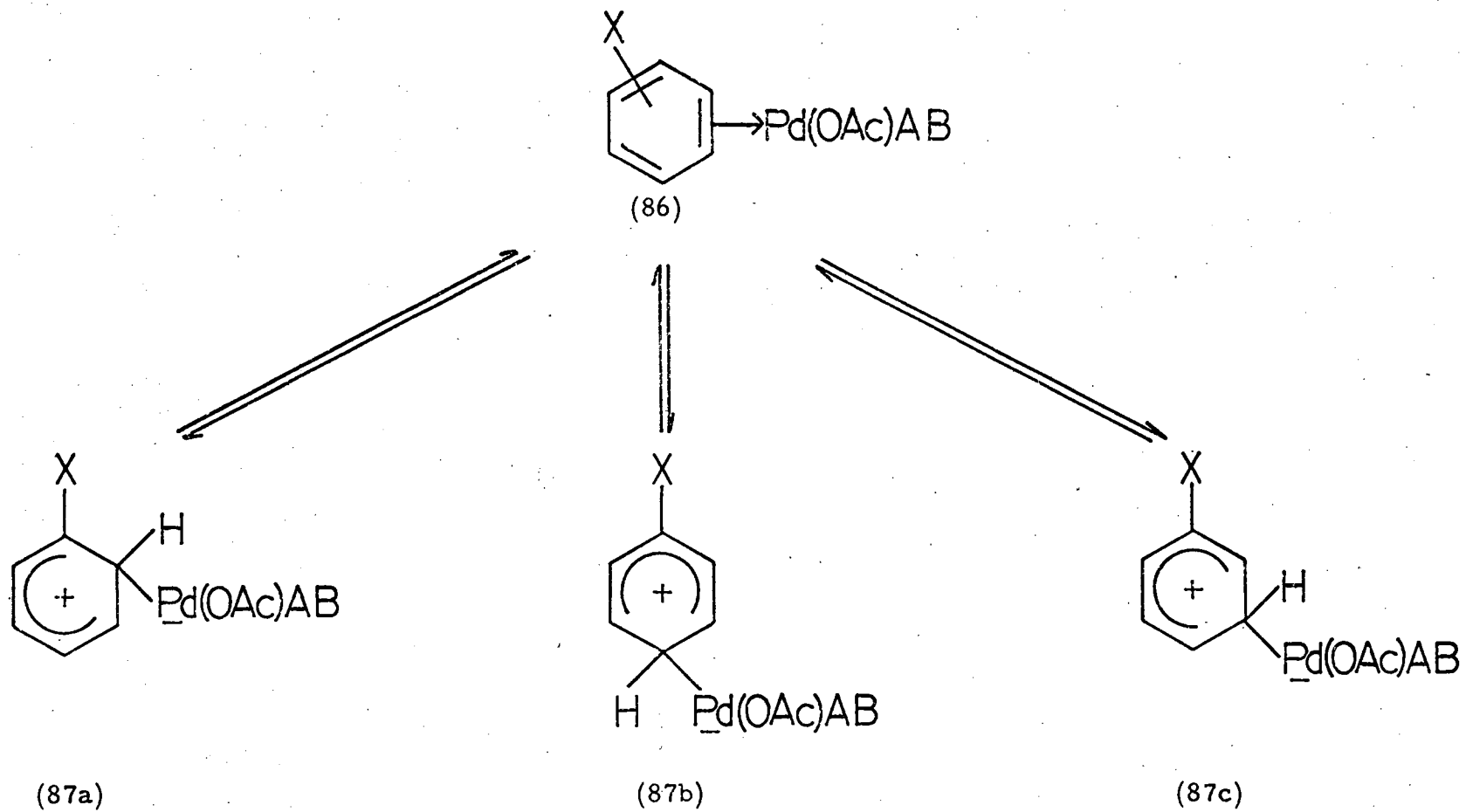


Electrophilic substitution by palladium (II) into the benzene ring can then occur followed by scission of the aromatic carbon-hydrogen bond in the zwitterionic species (87) to afford a  $\sigma$ -arylpalladium species (88) [Scheme 31].



Scheme 31

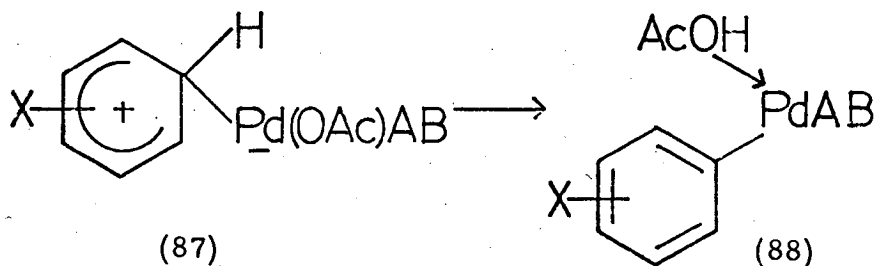




Scheme 32

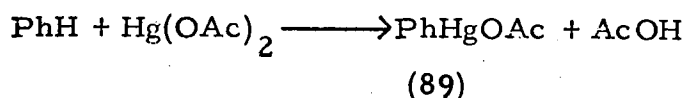
The product isomer distribution and the narrowness of the range of effects observed in the competitive arylations can be explained by considering the formation of the  $\sigma$ -arylpalladium species (88) and this applies to all four mechanisms since all involve  $\sigma$ -arylpalladium bond formation at some stage of the reaction. Consider electrophilic attack by palladium (II) on the  $\pi$ -bonded aromatic compound in (86). The palladium atom is associated with the ring as a whole and so each of the isomeric intermediates (87 a, b and c) is possible (Scheme 32). Charge separation has occurred in the isomeric palladated species (87a, b and c) and the most stable is the one in which these charges can be most easily accommodated. The effect of the positive charge depends on the nature and position of the substituent X, according to the criteria applied in electrophilic aromatic substitution reactions. The effect of negative charge on palladium in the isomeric species (87) is reduced by distribution of the electron density through vacant d-orbitals and by transfer to the electron-withdrawing acetate group. This causes the electronic effect of the aromatic substituent X to be less than in 'normal' electrophilic aromatic substitutions and thus the narrowness of the range of values observed for partial rate factors and reactivity of substituted benzenes is explained.

The next step, in all four mechanisms, is non-reversible rate-determining loss of a proton from the aromatic ring and an acetate group from palladium to afford (88).

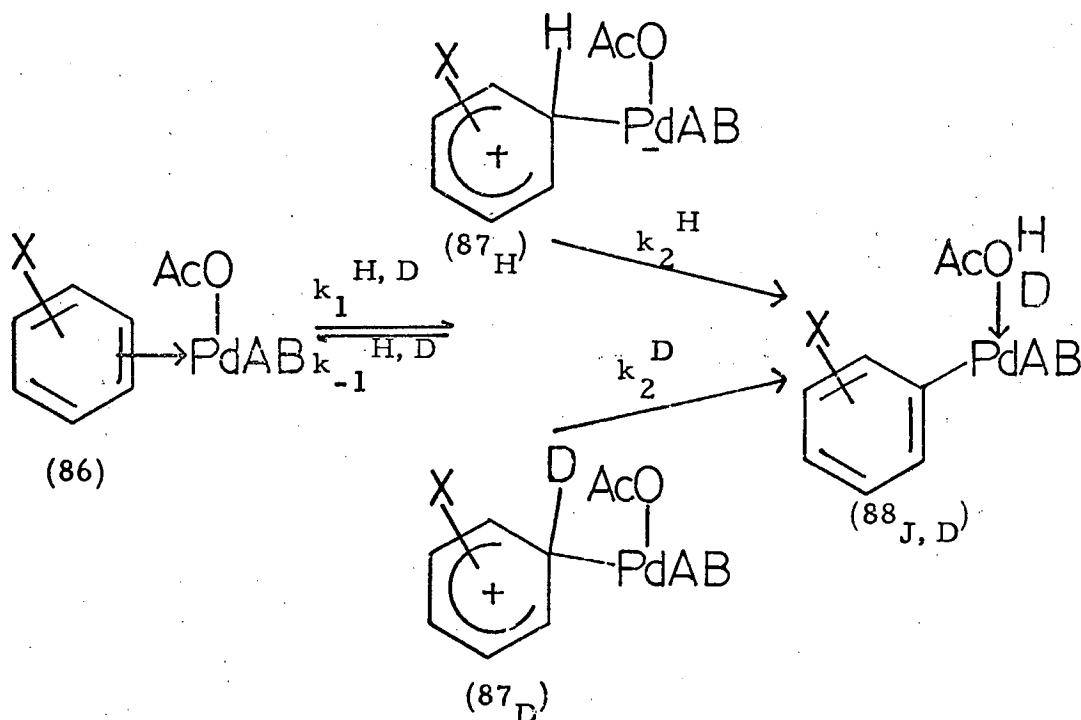


Re-aromatisation of a benzene ring usually has a low energy barrier so this step is not rate-determining. For this reason a primary kinetic isotope effect is not expected. However, Shue's results<sup>42</sup> suggest that re-aromatisation is rate-determining and irreversible.

There is a precedent for rate-determining re-aromatisation of a benzene ring and this in a system similar to the one under investigation. Thus, electrophilic mercuration occurs in the reaction of an aromatic compound with a mercury salt (e.g. mercuric acetate) with benzene.



A kinetic isotope effect, with benzene- $\text{d}_0$  and benzene- $\text{d}_6$  ( $k_{\text{H}}/k_{\text{D}} = 6.0$ )<sup>62</sup> was observed for formation of phenylmercuric acetate (89). This effect is attributed to the weakness of the carbon-mercury bond relative to that of the carbon-hydrogen bond. Such an explanation can be applied to formation of the palladium intermediate (88) [Scheme 33].

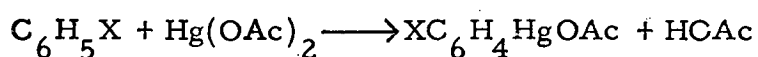


Scheme 33

If the carbon-palladium  $\sigma$ -bond is weak, the rate of reaction  $k_{-1}$  is significant relative to  $k_2$  and is independent of the presence of hydrogen or deuterium in (87). However,  $k_2^{\text{H}}$  is greater than  $k_2^{\text{D}}$  and if  $k_{-1}^{\text{H, D}}$  is comparable with  $k_2^{\text{D}}$ , a primary kinetic isotope effect will be observed because more protiated than deuterated molecules of (87) will proceed through to intermediate (88), the deuterated molecules being involved in the equilibrium  $[86 \rightleftharpoons 87]$ .

Another feature of mercuration common to the palladium (II)-assisted arylation is the narrow range of partial rate factors obtained from the mercuration of monosubstituted benzenes, although the range of effects is wider than that found in the palladium reaction under study (Table 33).<sup>62</sup>

Table 33    Partial Rate Factors for the Mercuration of  
Monosubstituted Benzenes<sup>62</sup>



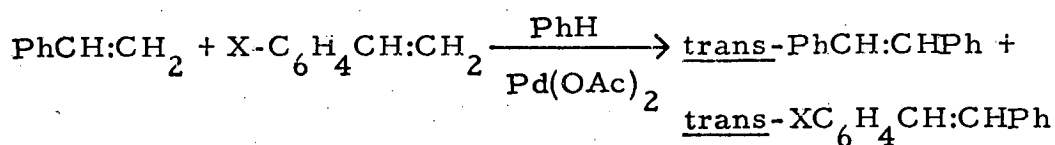
X	$f_{\text{o}}$	$f_{\text{m}}$	$f_{\text{p}}$
MeO	188	-	2310
Me	5.77	2.26	23.2
Cl	0.075	0.054	0.34

Thus, competitive arylation of alkenes assisted by palladium (II) shows that the aromatic compounds undergo electrophilic substitution by palladium (II) and that proposing re-aromatisation as the rate-determining step is feasible. All four mechanisms can accommodate these two proposals.

## 2.5 Competitive Alkenylations of Benzene

A series of palladium acetate assisted competitive alkenylations of benzene with styrene and a ring-substituted styrene was carried out, and the yields of each stilbene formed and the reactivity ratio of each substituted styrene to styrene are listed in Table 34.

Table 34     Competitive Alkenylations of Benzene with Styrene  
and Ring-Substituted Styrene



X	Stilbene (%)	Substituted Stilbene (%)	Reactivity Ratio ( $k_X/k_H$ )
4-Me	7.2	7.0	0.97 <sup>†</sup>
4-Me <sup>*</sup>	7.3	8.0	1.09 <sup>†</sup>
4-Me	2.1	1.9	0.88
4-Me <sup>*</sup>	2.1	2.1	0.97
4-Cl	2.6	2.0	0.75
3-CF <sub>3</sub>	2.9	3.1	1.06
3-CF <sub>3</sub> <sup>*</sup>	2.8	2.9	1.02

\* Palladium acetate batch 11; all other reactions, batch 10.

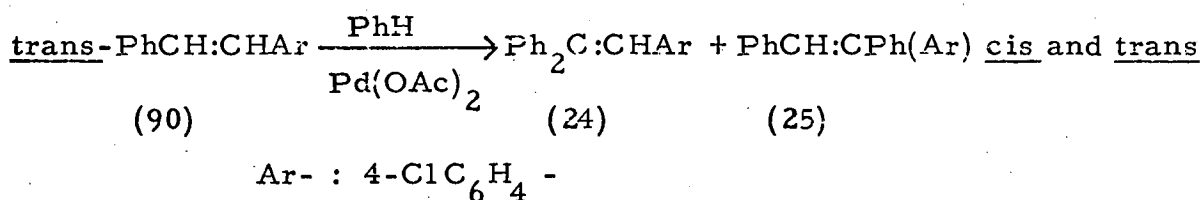
† Reaction time 20 min; all other reaction times 8 min.

These reactions show very little significant variation in reactivity ratio. The substituents in the styrene are further removed from the reaction coupling site than are substituents in the aromatic compounds and so the effect of the ring-substituents in styrene would be expected to be less than that of substituents in the aromatic compounds, all other things being equal.

A competitive alkenylation of benzene with styrene and 3,3-dimethylbut-1-ene was performed and the yields of phenylated alkenes were measured and the reactivity ratio calculated. The yield of trans-stilbene was 13.2% and of the tert-butylstyrene was

3.2% giving a reactivity ratio of 0.24. That phenylation of styrene occurs about four times as quickly as phenylation of 3,3-dimethylbut-1-ene is possibly due either to the preferential coordination of styrene to palladium or to the steric hindrance of attack of benzene on palladium by the *t*-butyl group of 3,3-dimethylbut-1-ene. No particular mechanism is favoured by these results.

When the phenylation of 4-chloro-trans-stilbene (90) in the presence of palladium acetate was carried out, two products, 2-(4-chlorophenyl)-1,1-diphenylethylene (24) and 1-(4-chlorophenyl)-1,2-diphenylethylene (25), were obtained by reaction at each olefinic carbon.



The ratio of the two products, (24)/(25), was found to be 1.2:1 from g.l.c. analysis by comparison of the peak heights of the two components with the peak heights of known amounts of each product. However, the possible error in the measurement of this ratio is definitely greater than 20% and so it is possible to conclude only that reaction at each olefinic site is very approximately equally facile. Both sites are sterically identical but are different electronically and so if a series of substituted trans-stilbenes were phenylated information would be obtained about the electronic nature of reaction at the alkene.

## 2.6 Effect of Reactant Ratio on the Phenylation of Styrene

Two groups of experiments were performed: the amount of styrene was increased relative to the other reactants; and the amounts of styrene and palladium acetate were increased together relative to the other reactants. A preliminary series of reactions was carried out with palladium acetate (batches 2A and 3A), the

product mixture being analysed for trans-stilbene, triphenylethylene and the alkene coupling product, 1,4-diphenylbuta-1,3-diene, and the results are listed in Table 35.

Table 35    Effect of Reactant Ratio on Product Distribution of Styrene Phenylation

Reactants (molar equiv.)			Products (%)			Reaction of Palladium (%)
B	S	P	<u>t</u> -stb	TPE	DPB	
100	1	1*	32.3	20.4	0	73.1
100	1	1*	39.7	14.3	0	68.3
100	1	1*	2.0	40.0	0	82.0
100	5	1*	19.1	3 <u>±</u> 1	7 <u>±</u> 1	32 <u>±</u> 3
100	10	1*	21.2	5 <u>±</u> 1	23 <u>±</u> 1	54 <u>±</u> 3
100	20	1*	8.5	0	10	18.5
100	1	1	51.1	3.5	0	58.1
100	1	1	52.7	9.5	0	71.7
100	1.25	1.25	37.9	12 <u>±</u> 1	1 <u>±</u> 1	63 <u>±</u> 3
100	1.25	1.25	35.4	17 <u>±</u> 1	1 <u>±</u> 1	70 <u>±</u> 3
100	1.66	1.66	23.8	16 <u>±</u> 1	1 <u>±</u> 1	57 <u>±</u> 3
100	1.66	1.66	48.4	6 <u>±</u> 1	1 <u>±</u> 1	61 <u>±</u> 3
100	2.5	2.5	30.8	6 <u>±</u> 1	1 <u>±</u> 1	44 <u>±</u> 3

\* Palladium acetate batch 2A. Batch 3A used in all other reactions.  
 B:- benzene; S:- styrene; P:- palladium acetate; t-stb:- trans-stilbene; TPE:- triphenylethylene; DPB:- 1,4-diphenylbuta-1,3-diene.

Unfortunately, absolute reliance cannot be placed in these results because, at that time, it was not possible to obtain consistent results in any styrene phenylation. However, certain trends can be identified.

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene

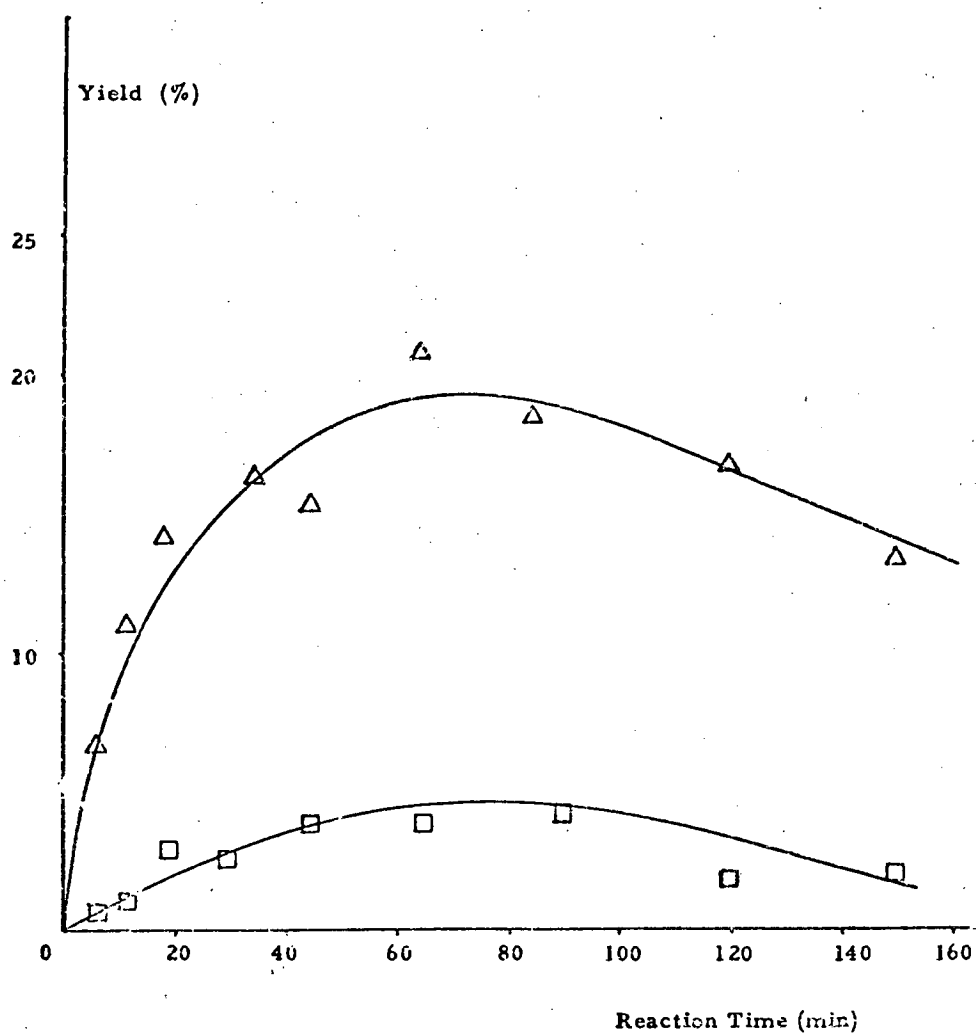
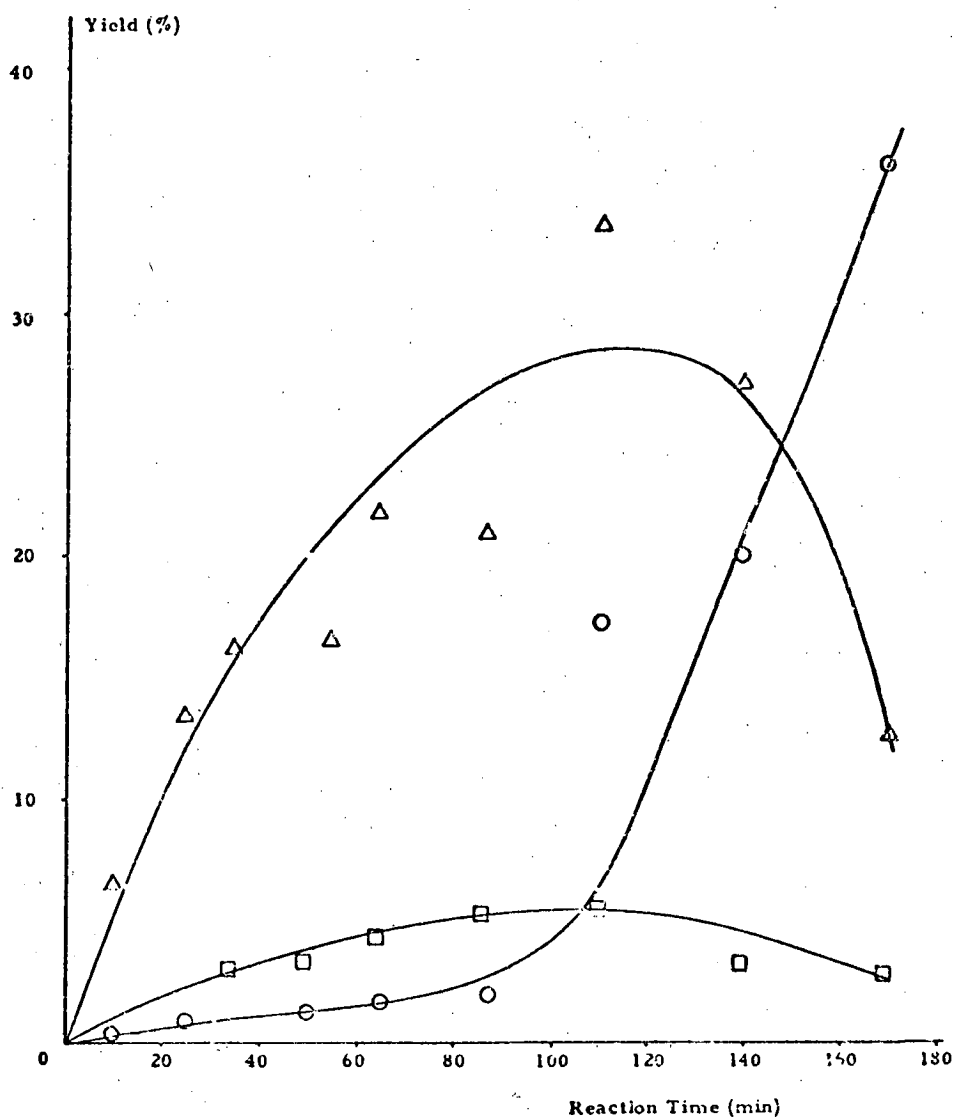


Figure 6a



Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene

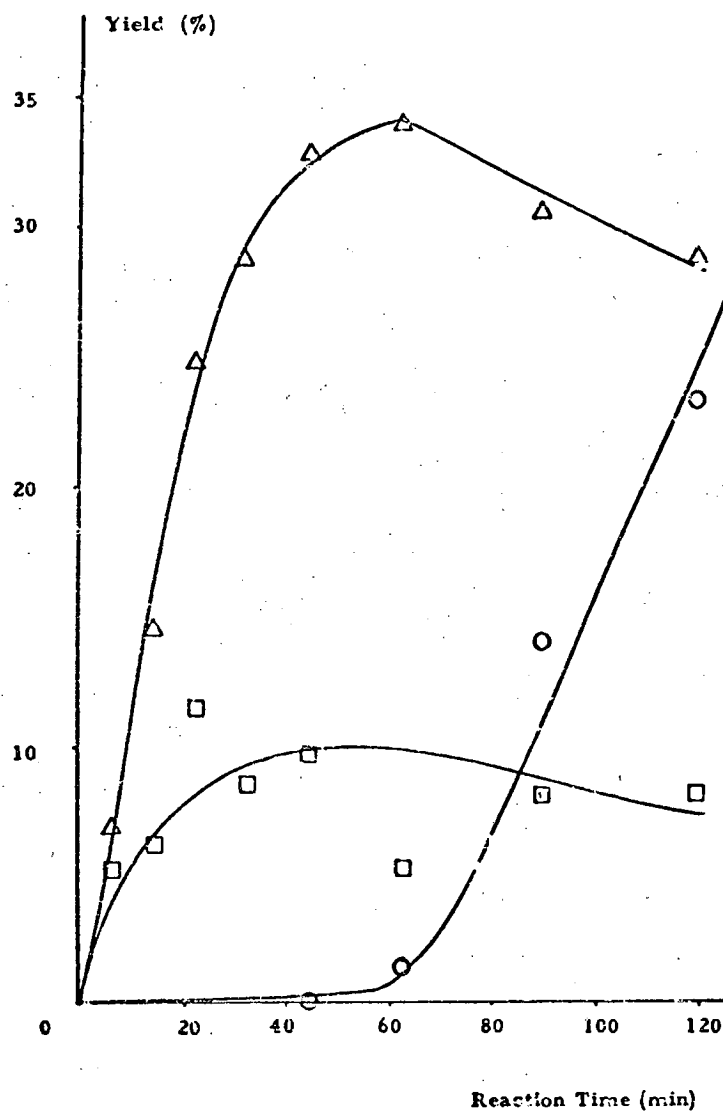


PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 1 : 1

- △ trans-stilbene
- triphenylethylene
- 1,4-diphenylbuta-1,3-diene

Figure 6b

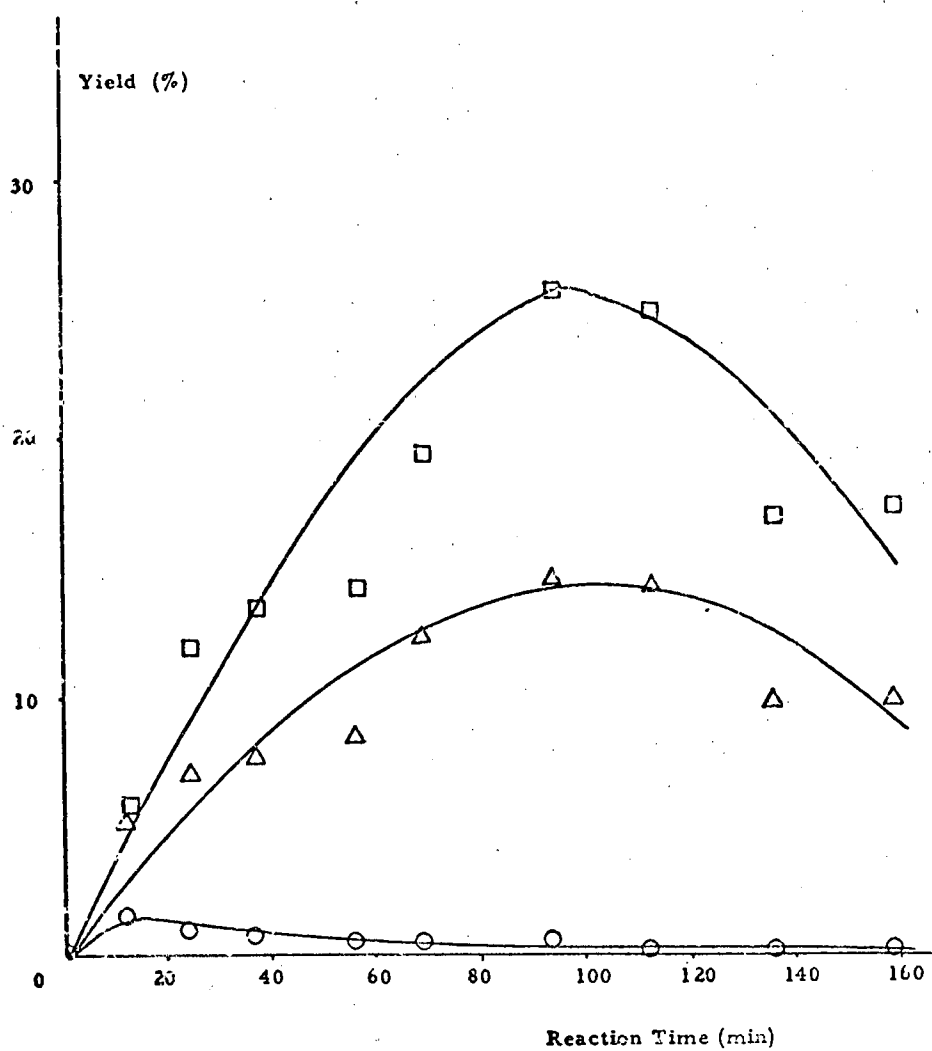
Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene



- △ trans-stilbene  
 ○ triphenylethylene  
 □ 1,4-diphenylbuta-1,3-diene

Figure 6c

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene



PhH:styrene:Pd(OAc)<sub>2</sub>

100 : 5 : 1

- Δ trans-stilbene  
 ○ triphenylethylene  
 □ 1,4-diphenylbuta-1,3-diene

Figure 6d

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene

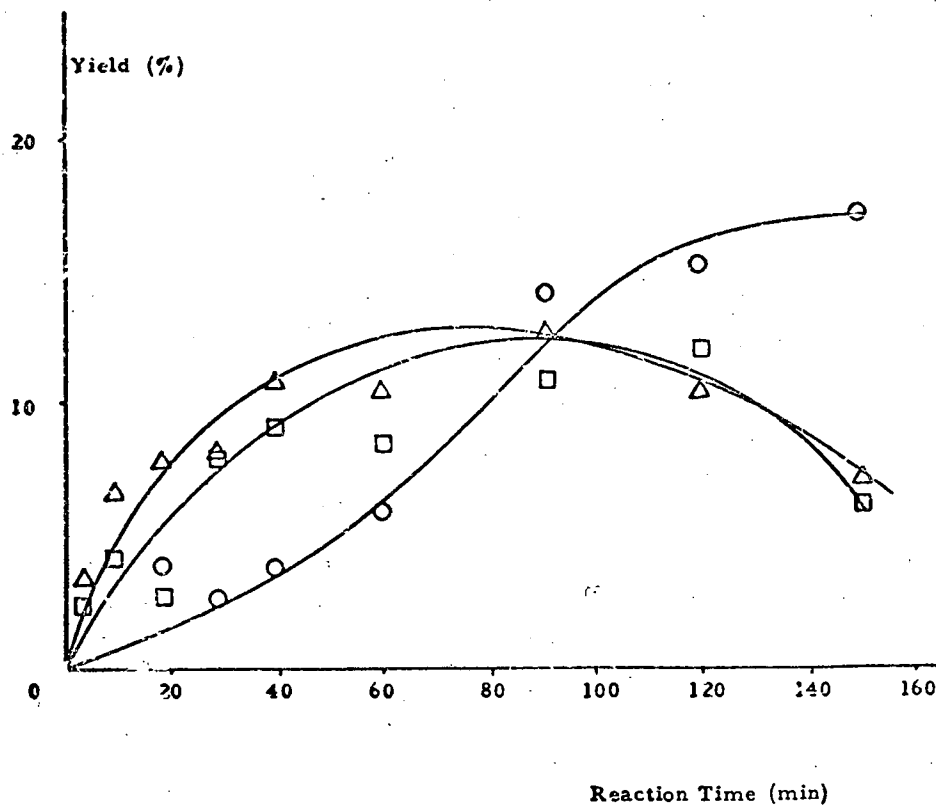
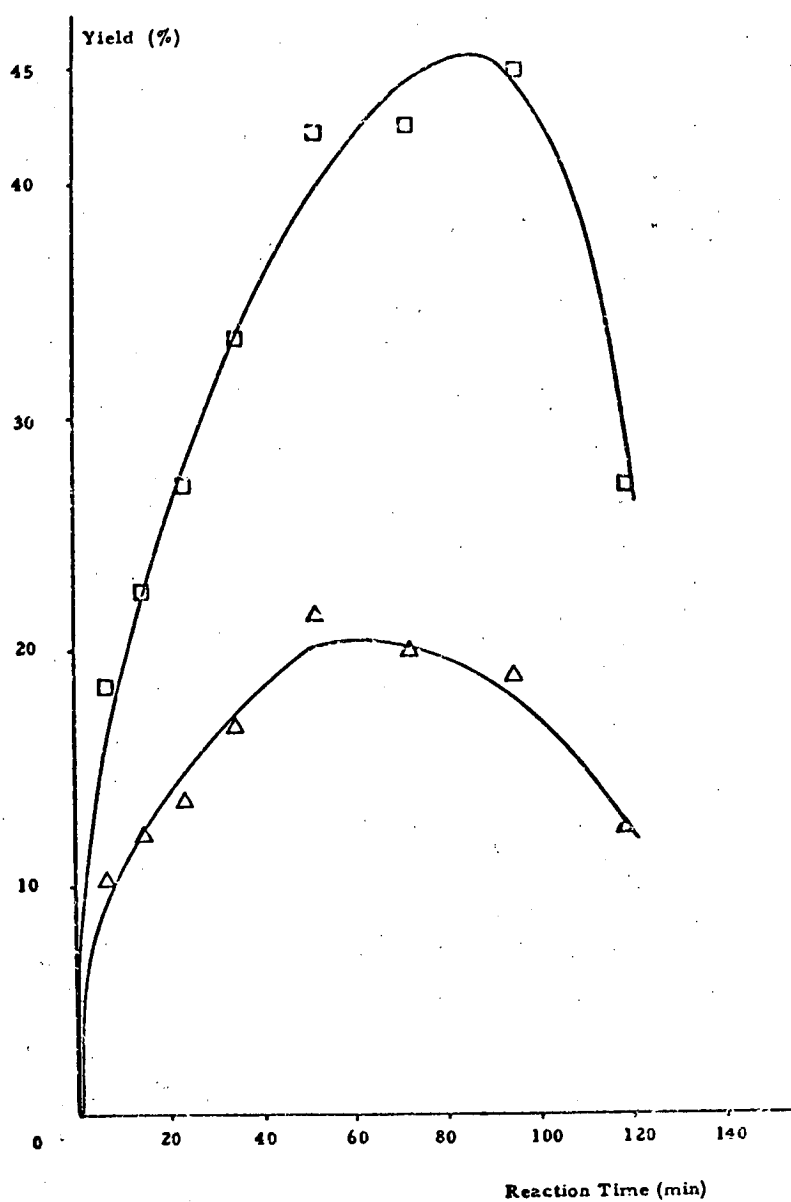


Figure 6e

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene

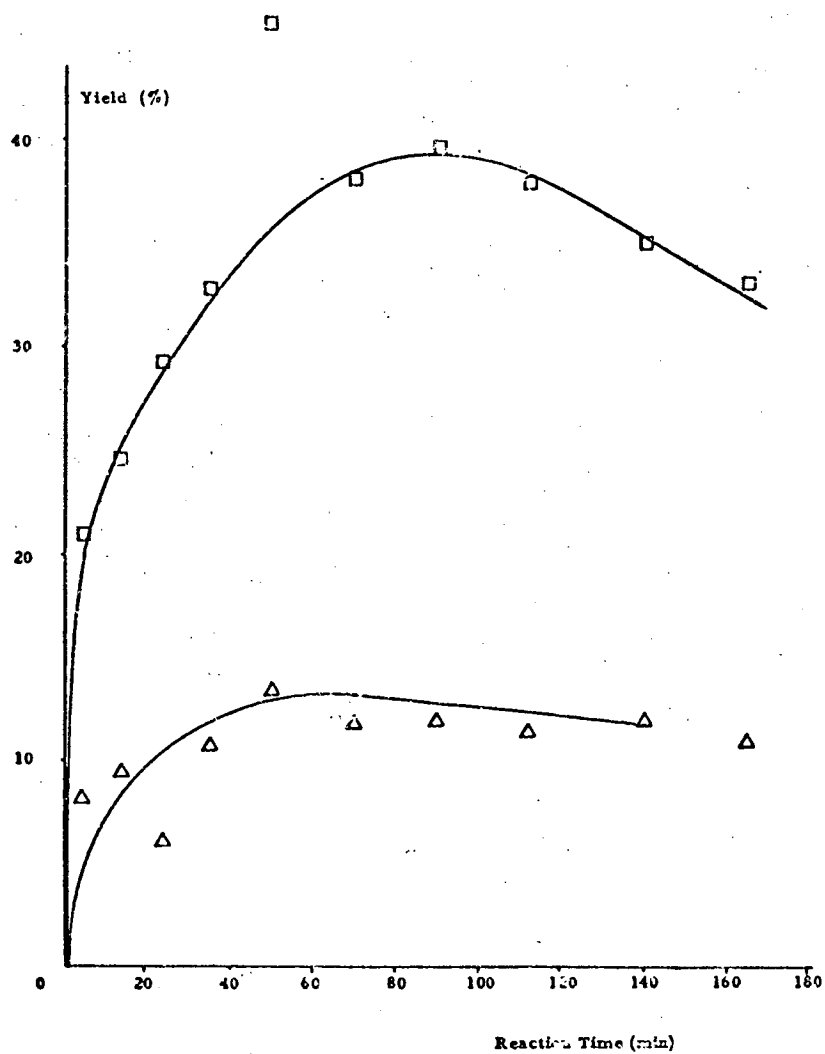


PhH:styrene: Pd(OAc)<sub>2</sub>  
100 : 10 : 1

- Δ trans-stilbene  
□ 1,4-diphenylbuta-1,3-diene

Figure 6f

Effect of Reactant Ratio on Product Distribution  
in the Phenylation of Styrene



PhH:styrene:Pd(OAc)<sub>2</sub>  
100 : 20 : 1

- Δ trans-stilbene  
□ 1,4-diphenylbuta-1,3-diene

Figure 6g

If those reactions in which only the amount of styrene is changed relative to the other reactants are considered, it is seen that, as the styrene concentration increases, there is a marked reduction in the formation of trans-stilbene and of triphenylethylene compared with the 'normal' phenylation. Also 1,4-diphenylbuta-1,3-diene is formed in significant amounts. This is a known reaction and its occurrence in styrene phenylation has been reported by Moritani<sup>15</sup> and Shue.<sup>43</sup> It was reasonable to expect that triphenylethylene formation would be decreased because, at all times throughout the reaction, styrene is in excess of trans-stilbene, a situation which does not arise in the 'normal' phenylation.

When both styrene and palladium acetate were changed together, little alkene coupled product was obtained but the yields of trans-stilbene and triphenylethylene vary without showing any definite trend.

This preliminary study indicated that this work was worthy of more attention once the problem of consistency of product yields was solved.

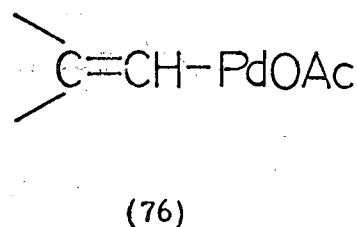
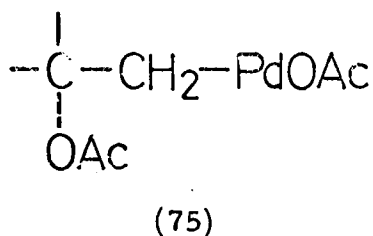
When solved, a kinetic study of the effect of changing the amount of styrene relative to the other reactants, and of changing the amounts of styrene and palladium acetate (batch 11) relative to the other reactants was performed under nitrogen. However, it is thought that various amounts of oxygen were present because the total percentage reaction of palladium was, in some cases, about 100%. Table 36 shows the composition of the reaction mixtures and Figure 6 illustrates the appearance and disappearance of the products, trans-stilbene, triphenylethylene and 1,4-diphenylbuta-1,3-diene.

A comparison of Figure-6b ('normal' phenylation) with Figures 6d, 6f and 6g (increase in styrene relative to the other reactants) shows that as the styrene concentration increases 1,4-diphenylbuta-1,3-diene becomes the predominant product, the triphenylethylene yield being virtually zero except in the 'normal' phenylation.

**Table 36**     Composition of Reaction Mixtures in the Kinetic Study of the Effect of Reactant Ratio on the Phenylation of Styrene (molar equiv.)

Reaction number	1	2	3	4	5	6	7
Figure	6a	6b	6c	6d	6e	6f	6g
Palladium acetate	1	1	2	1	5	1	1
Styrene	1	1	2	5	5	10	20
Benzene	200	100	100	100	100	100	100
Acetic acid	100	50	50	50	50	50	50

Figures 6f and 6g show that the initial rate of formation of trans-stilbene is greater than in the phenylation of styrene under 'normal' conditions (Figure 6b) and that the rate of alkene coupling is even faster. It has already been assumed that the alkene coupling reaction occurs through the acetoxymethylpalladium adduct (75) or the  $\sigma$ -alkenylpalladium species (76).



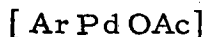
The increased rate of butadiene formation follows from this assumption. Since the styrene concentration has been increased greatly there is more free styrene to react with adduct (75), or species (76), which will itself be formed to a greater extent, thereby increasing the rate of butadiene formation. The non-appearance of triphenylethylene is due simply to the vast excess of styrene relative to trans-stilbene.

If alkene arylation occurs through the same complex as operates in alkene coupling it is feasible that the rate of formation of stilbene would be increased because of the greater formation



of the reactive complex, (75) or (76).

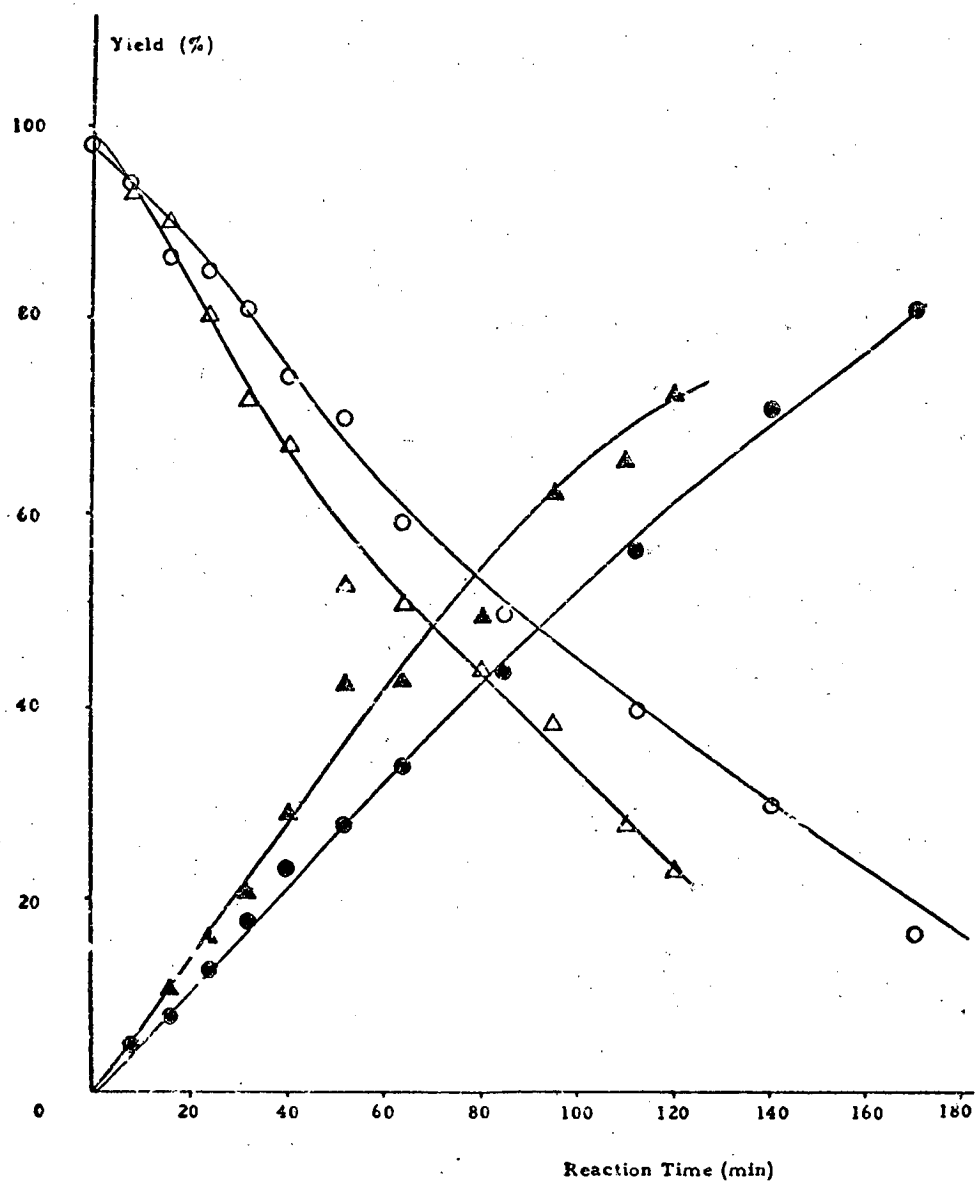
However, if alkene arylation occurs through a  $\sigma$ -aryl-palladium complex (3), then for the increased rate of stilbene formation, illustrated by Figures 6f and 6g, two explanations need be considered.



(3)

Firstly, if the rate of formation of the  $\sigma$ -aryl species (3) were actually faster than the rate of reaction of styrene with the complex (3), any increase in the styrene concentration would then give an increase in the rate of stilbene formation. This explanation is not consistent with the primary kinetic isotope effect observed by Shue<sup>42</sup> in the competitive arylation of styrene with benzene- $\text{d}_0$  and benzene- $\text{d}_6$  which suggests that the rate of formation of the  $\sigma$ -aryl-palladium species (3) is slower than the rate of reaction of this species with styrene. Secondly, the possibility exists that the presence of styrene in the reaction mixture could enhance formation of the  $\sigma$ -aryl species (3). There are two possibilities for the enhancement of  $\sigma$ -arylpalladium complex formation: either a trans-effect or a cis-effect due to styrene. Replacement of the ligand trans to  $\pi$ -bonded styrene by benzene gives a complex in which styrene and benzene are trans to each other. Isomerisation of the trans-complex to the cis-complex followed by coupling of the two organic moieties affords trans-stilbene. Alternatively, replacement of the ligand cis to styrene gives a complex with styrene and benzene cis to each other and coupling of these two species yields the product. There is no evidence to suggest the involvement of a styrene cis-effect in palladium (II)-assisted reactions. The involvement of an alkene trans-effect followed by trans-to-cis isomerisation has been postulated in the Wacker process but there is no evidence to suggest that this effect occurs in styrene phenylation. It will be shown later that alkene phenylation assisted by palladium acetate can be explained without the need to invoke either of the two effects described above.

# Phenylation of trans-Stilbene



- trans-stilbene
  - triphenylethylene
  - Δ trans-stilbene
  - ▲ triphenylethylene
- } under atmosphere of nitrogen

Figure 7

Mechanism 1 (p. 92) basically Moritani's mechanism except that the rate-determining step is aryl to palladium  $\sigma$ -bond formation, could explain an increased rate of trans-stilbene formation as the styrene concentration is increased. The situation in Mechanism 1 implies the need for styrene to be present before reaction between benzene and palladium can occur. This situation is similar to that described for the possible cis-effect of styrene and as stated above alkene phenylation can be explained without invoking this cis-effect.

Figure 6c shows increased rates of formation of trans-stilbene and 1,4-diphenylbuta-1,3-diene over the 'normal' phenylation. This result is explicable by all four mechanisms (see p. 92). It is expected that both aryl and alkene complex formation would be increased thus leading to the increased rates of formation of stilbene and alkene coupled product.

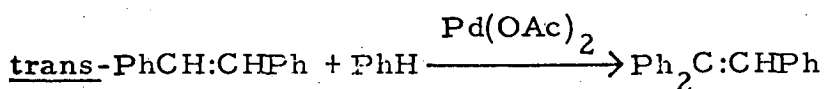
There is at present no explanation for the results illustrated by Figures 6a and 6e.

The investigations into the effect of reactant concentration or styrene phenylation assisted by palladium acetate lead to the conclusion that the reaction occurs via the acetoxyalkylpalladium adduct (75) or the  $\sigma$ -alkenyl species (76).

## 2.7 Phenylation of trans-Stilbene

A series of phenylation reactions of trans-stilbene assisted by palladium acetate was carried out and the disappearance of trans-stilbene and the appearance of triphenylethylene were determined by g.l.c. The results are shown in Table 37 and Figure 7. The yields of triphenylethylene from trans-stilbene are greater than those of stilbene obtained from styrene (Table 8, p. 69) indicating the greater selectivity of trans-stilbene towards phenylation.

Table 37     Palladium Acetate Assisted Phenylation of  
trans-Stilbene



Pd(OAc) <sub>2</sub> Batch	Reaction Time (min)	Stilbene (%)	TPE (%)
10	120	23.0	72.4
10	170	16.3	81.2 <sup>†</sup>
10	180	0	94.3
11	218.5	0	97.8
10	1160	1.0	100.2 <sup>†</sup>
11	1200	0	78.0

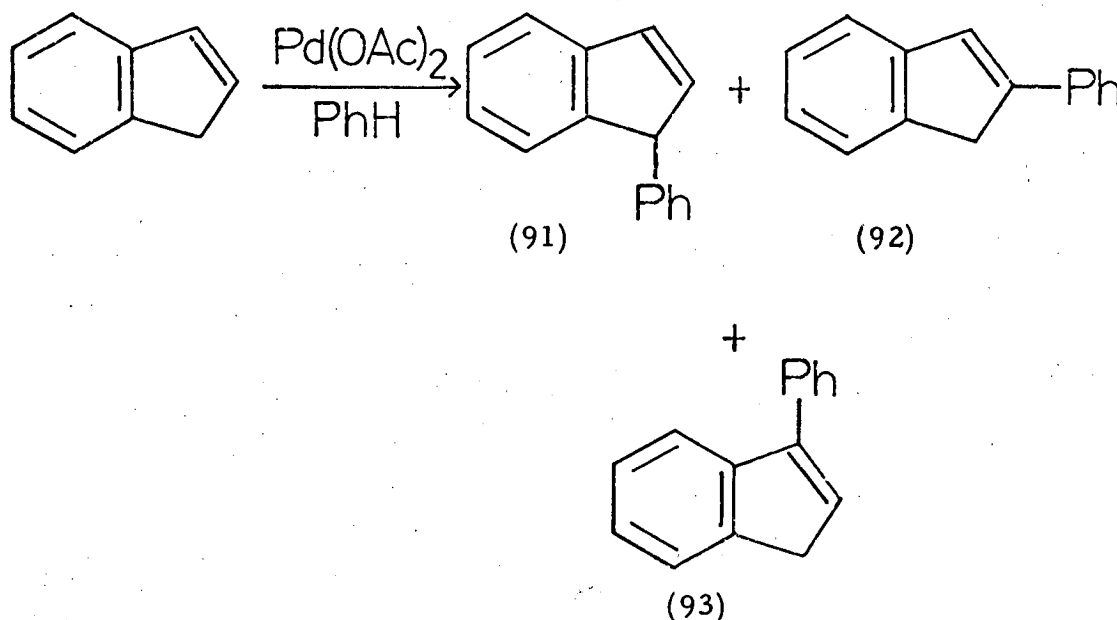
TPE:- triphenylethylene

† Reaction carried out under nitrogen.

A comparison of the rates of phenylation of styrene and trans-stilbene (Figures 2 and 7) shows them to be similar. However, it has already been noted that in the phenylation of styrene, triphenylethylene formation becomes important only when the styrene concentration is low. These results are explained by coordination of styrene with palladium being more facile than coordination of trans-stilbene to palladium. Only when the styrene concentration is low would coordination of trans-stilbene to palladium become important. This has no effect on the rate of reaction because that is determined by reaction of arene with a palladium species. The difference in the ease of coordination of alkene to palladium and the similar rates of phenylation of styrene and trans-stilbene can adequately be explained by the four mechanisms postulated.

## 2.8 Phenylation of Indene

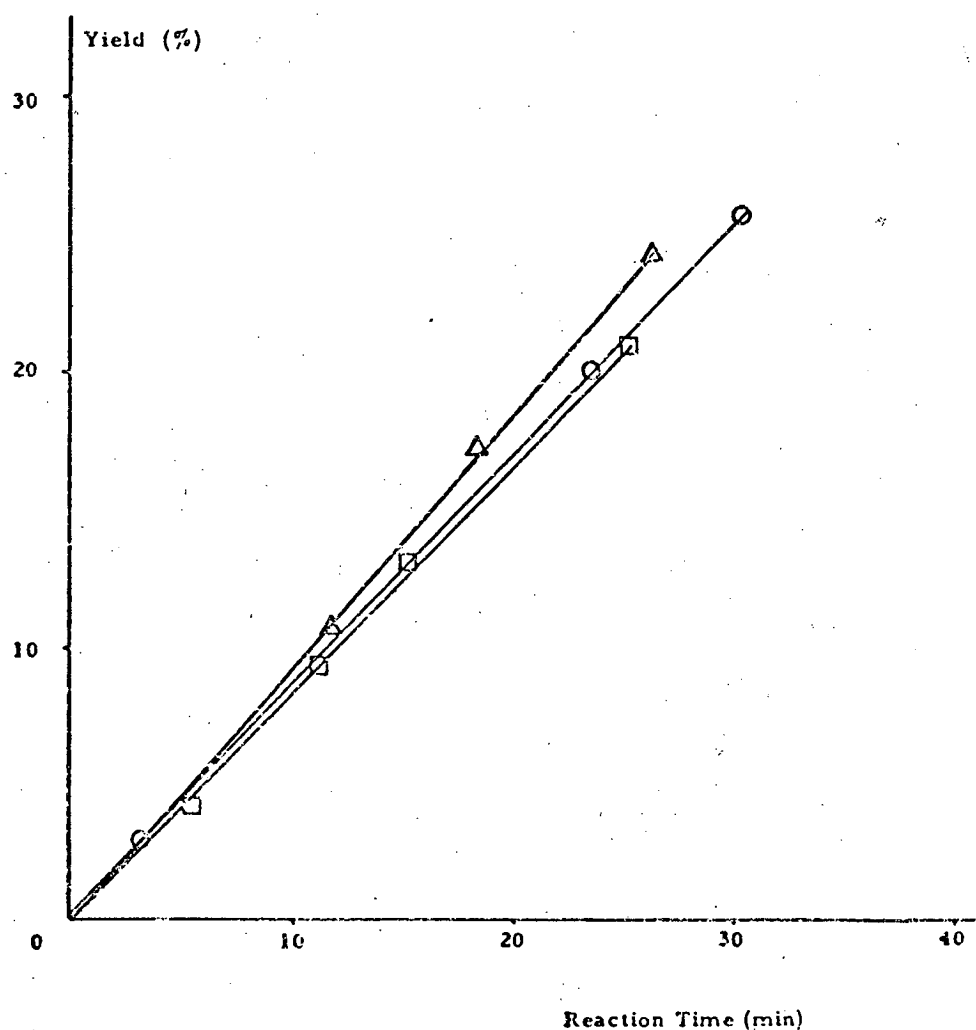
As indene is electronically similar to styrene it was considered worthwhile to attempt its phenylation. The phenylation of indene assisted by palladium acetate produced three phenylated products; 1-phenylindene (91), 2-phenylindene (92) and 3-phenylindene (93), their yields being in the ratio 1:4:1.



None of the four mechanisms described previously can satisfactorily explain the product distribution obtained and so further investigations of this system are necessary.

## 2.9 Other Mechanistic Studies

It has been proposed by many workers, including Davidson,<sup>9</sup> Norman<sup>59</sup> and Eberson,<sup>87</sup> that biaryl formation proceeds via a  $\sigma$ -aryl palladium acetate, the rate-determining step involving  $\sigma$ -bond formation between the arene and palladium. In this study an attempt was made to effect phenyl coupling by the reaction of benzene in acetic acid in the presence of palladium acetate. However, the yield of biphenyl obtained after reaction at  $77^\circ$  for 3 hours was only 6% which implies that phenylpalladium acetate is formed only very slowly. To check whether this thesis were correct a similar phenyl coupling reaction was performed but after reaction for 1.25 h



stilbene

- 'normal' phenylation of styrene
- △ Run 1 styrene addition to reaction
- Run 2 mixture 4.9(a)

Figure 8

styrene was added to the reaction mixture. If phenylpalladium acetate were formed at a rate greater than that suggested by the very small biphenyl yield, reaction of styrene would be expected to give an immediate and large yield of trans-stilbene. The results of this reaction are illustrated in Figure 8 which shows that the rate of trans-stilbene formation is, within experimental error, the same as that found for styrene phenylation carried out by the 'normal' procedure.

From this can be concluded that phenylpalladium acetate is not the intermediate involved in styrene phenylation and that an intermediate formed by reaction between styrene and palladium acetate is involved.

## 2.10 Attempts to Study Styrene Phenylation by Spectroscopic Techniques

### (a) Nuclear Magnetic Resonance Spectroscopy

It was considered worthwhile to attempt to study styrene phenylation by observing changes in the resonances of the olefinic protons at 100MHz both in the absence and presence of palladium acetate. It was hoped that complexing between styrene and palladium acetate would result in changes in the olefinic proton resonances. No changes were observed. This can be explained either by the non-occurrence of complexing between styrene and palladium acetate or by the complex formed being in a very rapid equilibrium with the free reactants. However, it is also possible that the extent of complexing is too small for its effect to be noticed or that no shift in the resonances of the vinylic protons occurs on complexing.

### (b) Ultra-Violet Spectroscopy

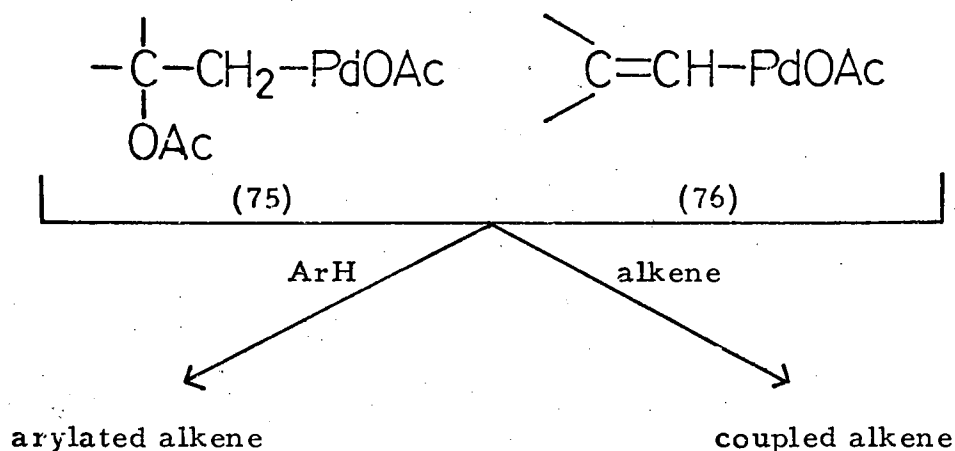
No shift in the styrene absorption from 255 m $\mu$  and only a small increase (about 4%) in the molar absorptivity ( $\epsilon_{\text{max.}}$  ca. 6900)

was observed on addition of palladium acetate to styrene in acetic acid at 80°. This can be explained by the same four reasons that were applied to the n.m.r. investigation: firstly, that no complexing occurs between styrene and palladium (II); secondly, that there is a rapid equilibrium between the complex and the free reactants; thirdly, that the extent of complexing is too small for its effect to be noticed and fourthly, that no shift in the absorption occurs on complexing.

A qualitative study of styrene phenylation was made but only absorptions due to the products, trans-stilbene and 1,4-diphenylbuta-1,3-diene were observed.

## 2.11 The Mechanism of Palladium (II)-Assisted Arylation of Alkenes

The mechanism proposed, from this study, for the palladium (II)-assisted arylation of alkenes is reaction of the alkene with palladium (II) to give either the acetoxyalkyl complex (75) or the  $\sigma$ -alkenyl complex (76).<sup>†</sup> The alkene coupling reaction is envisaged as occurring through the same intermediate, [(75) or (76)], which is involved in alkene arylation [Scheme 34].



Scheme 34

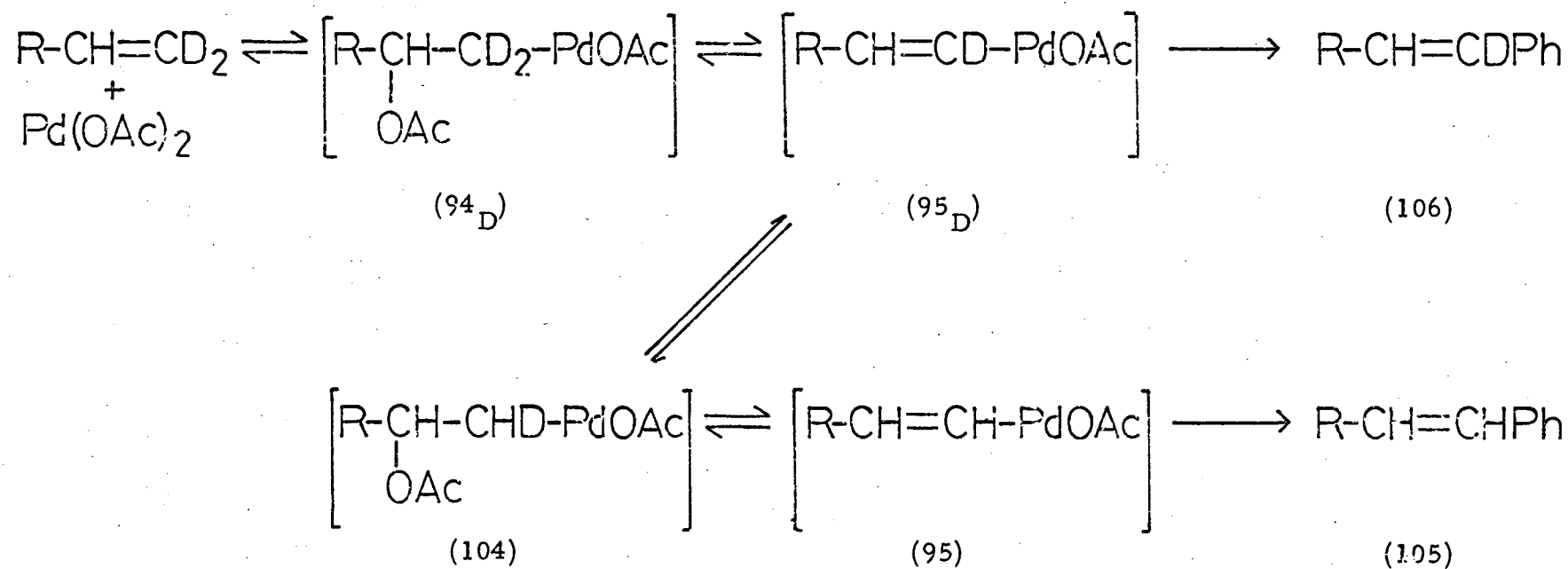
<sup>†</sup> It is also possible that alkene arylation occurs via a  $\sigma$ -aryl-palladium species, if its formation is enhanced by the presence of alkene, as discussed previously (p. 105). There is, however, no evidence for this occurrence in palladium-assisted alkene arylation.



Scheme 35 illustrates the proposed mechanism, the reaction occurring through either the alkyl complex (94) or the alkenyl complex (95). Addition of the alkene to palladium acetate gives the adduct (94). Reaction of adduct (94) with the aromatic compound proceeds via the  $\pi$ -complex (96), the zwitterionic species (97) and the  $\sigma$ -alkyl- $\sigma$ -aryl species (98),  $[(96) \rightleftharpoons (97) \rightarrow (98)]$  being analogous to two steps  $[(86) \rightleftharpoons (88)]$  in Scheme 31 (p.96). Loss of acetic acid from the  $\sigma$ -alkyl- $\sigma$ -aryl complex (98) must occur before loss of acetic acid and palladium (0), otherwise the substituted ethane (99) would be formed. Mass spectral analysis of reaction mixtures showed this ethane (99) was not among the products. Loss of acetic acid from intermediate (98) affords the  $\sigma$ -alkenyl- $\sigma$ -aryl species (100) which yields the arylated product (101) by attack of the aryl group on the olefinic carbon bonded to palladium. A similar sequence of reactions  $[(95) \rightleftharpoons (102) \rightleftharpoons (103) \rightarrow (100) \rightarrow (101)]$  accounts for formation of arylated alkene (101) via the  $\sigma$ -alkenyl-palladium species (95).

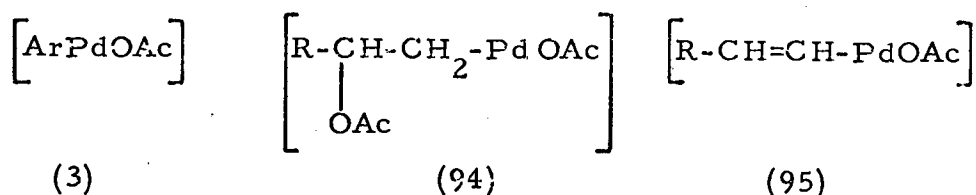
That reaction of the acetoxy adduct (94) to the  $\sigma$ -alkenyl species (95) is irreversible can be deduced from a result obtained by Moritani and co-workers.<sup>24, 25</sup> The phenylation of  $\beta, \beta$ -di-deuterostyrene produced solely monodeuterated stilbene. If equilibrium existed between species (94) and (95),  $\beta, \beta$ -dideuteroalkene would afford the dideuteroacetoxy adduct ( $94_D$ ) and the  $\beta$ -deuteroalkenyl species ( $95_D$ ) by loss of deuterated acetic acid [Scheme 36]. Re-combination of the deuterated species ( $95_D$ ) would be much more likely with protiated acetic acid than with the deuterated acetic acid formed because the protiated acid is in at least 50-fold excess. This would lead to the production of monodeuterated acetoxy adduct (104) which is capable of undergoing reaction to give stilbene- $d_0$  (105) and stilbene- $d_1$  (106). By the same reasoning step (98) to (100) must also be irreversible.

It is not possible, however, to discriminate between reaction through the acetoxy adduct (94) and the alkenyl species (95). The



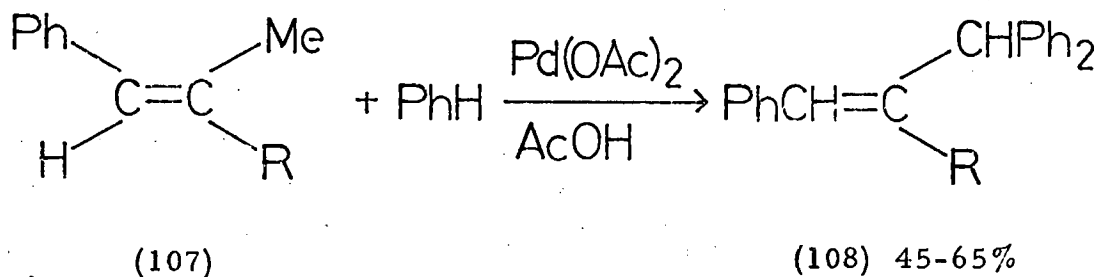
Scheme 36

mechanism (Scheme 35) satisfactorily explains the palladium (II)-assisted arylation of alkenes as performed in the current study. However, this does not imply that alkene arylation assisted by palladium acetate cannot occur through a  $\sigma$ -arylpalladium intermediate (3), rather than through the two species described, (94) and (95) under certain reaction conditions.



It is accepted that arylation of alkenes via reaction of arylmercuric acetate and palladium acetate is likely to occur through the  $\sigma$ -aryl species (3) but this is likely to be due to the much increased facility of  $\sigma$ -bond formation between the aryl group and palladium acetate.

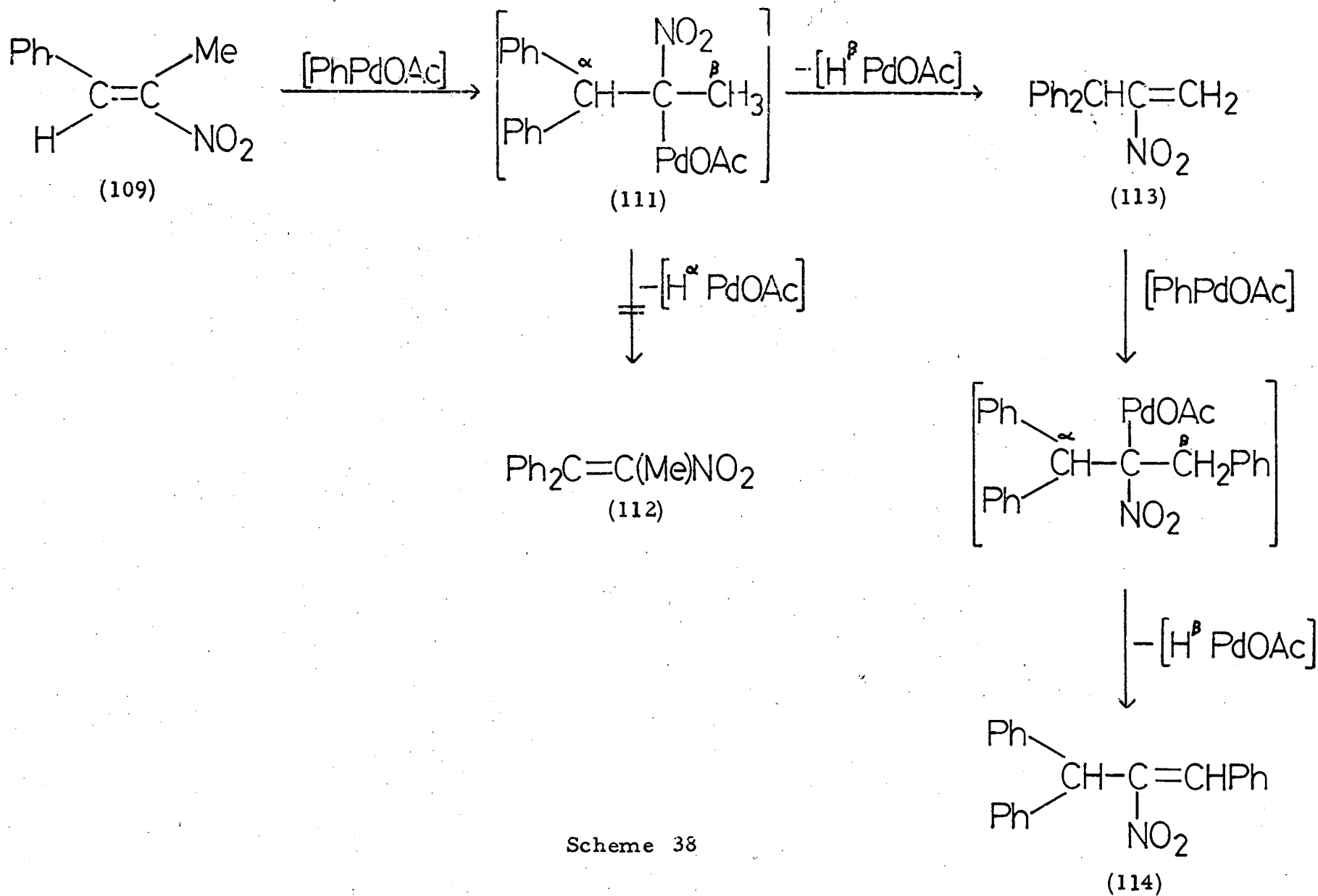
Another system in which alkene phenylation is proposed to occur via a  $\sigma$ -arylpalladium species, reported recently by Yamamura *et al.*,<sup>65</sup> involves reaction of  $\beta$ -substituted- $\beta$ -methylstyrenes (107) with benzene in the presence of palladium acetate to produce the corresponding  $\beta$ -substituted- $\beta$ -diphenylmethylstyrenes (108), [Scheme 37].



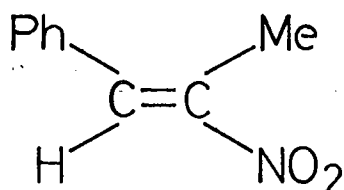
R:- NO<sub>2</sub>; COOH; COOMe; Ph; p-MeOC<sub>6</sub>H<sub>4</sub> and PhCH<sub>2</sub>

Scheme 37

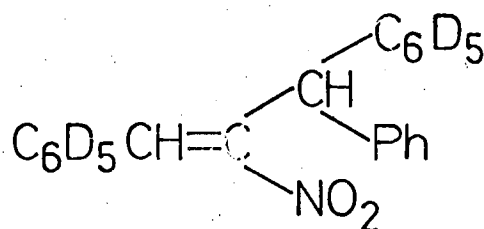
All investigative work was performed with  $\beta$ -methyl- $\beta$ -nitrostyrene (109). Direct phenylation of the methyl group was eliminated by the isolation of product (110) when the reaction was carried out using hexadeuterobenzene.



Scheme 38



(109)

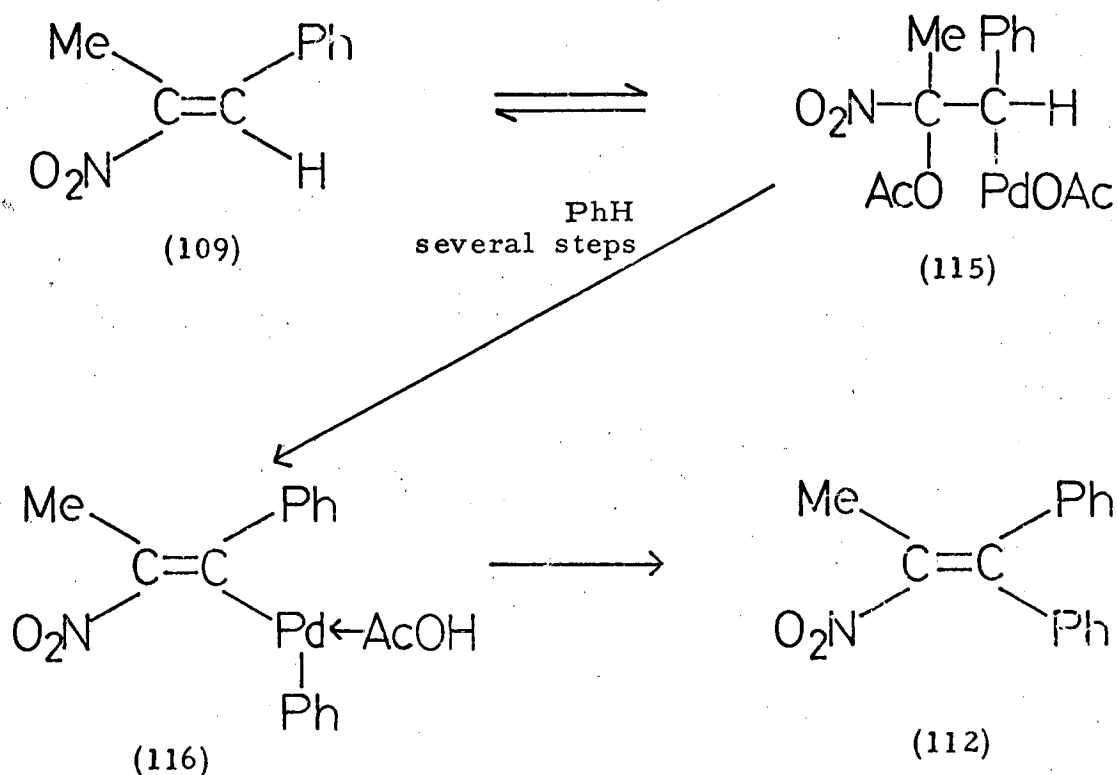


(110)

A mechanism invoking the intermediacy of  $\sigma$ -phenylpalladium acetate was proposed, [Scheme 38]. cis-Addition of phenylpalladium acetate across the olefinic double bond affords adduct (111) from which loss of hydridopalladium acetate by a cis-mechanism can occur to give two possible products, (112) and (113), by loss of  $\text{H}^\alpha$  or  $\text{H}^\beta$  respectively. The initial communication reported that phenylation of the nitrostyrene (109) afforded 1,1-diphenyl-2-nitropropene (112) but subsequent work showed that isolation of this compound was irreproducible and also that a small amount of 3,3-diphenyl-2-nitropropene (113) was formed. cis-Addition of phenylpalladium acetate to the propene (113) followed by cis-elimination of hydridopalladium acetate affords the final product (114). That the final product, 2-nitro-1,3,3-triphenylpropene (114) could be formed from the propene (113) was also demonstrated. Yamamura suggested that steric interaction prevented cis-elimination of  $\alpha$ -hydridopalladium acetate from adduct (111) from occurring.

It is not possible to explain the results described above on the basis of phenylation through either species (94) or (95) as described in Scheme 35. By analogy with Scheme 35,  $\beta$ -methyl- $\beta$ -nitrostyrene (109) would give the alkyl complex (115), reaction of which with benzene through the  $\sigma$ -alkenyl- $\sigma$ -arylpalladium species (116) would afford 1,1-diphenyl-2-nitropropene (112) [Scheme 39].

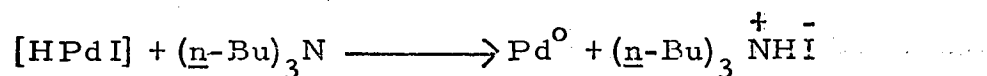
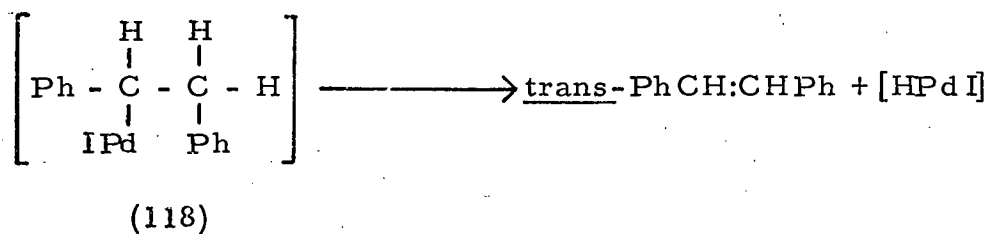
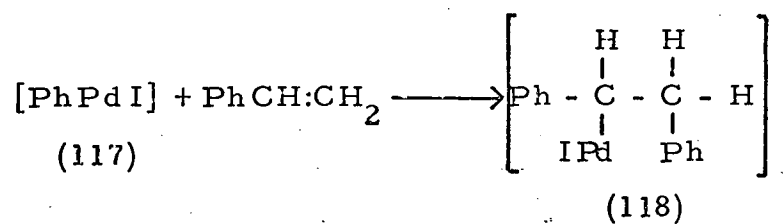
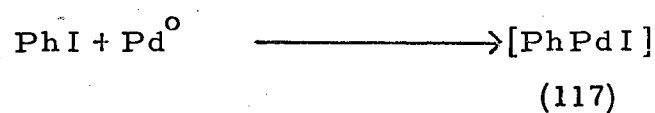
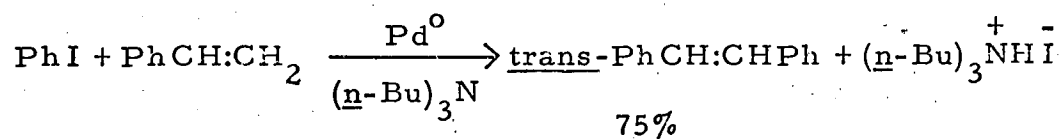
It is worth noting again that Yamamura's mechanism [Scheme 38] is based solely on the results of experiments performed with the  $\beta$ -nitrostyrene (109). The presence of the nitro-group will reduce markedly the availability of the  $\pi$ -electrons of the olefinic



Scheme 39

double bond for donation to palladium, thereby inhibiting the formation of alkyl species (115). Reaction through a  $\pi$ -allyl complex is unlikely in the presence of a nitro group because the availability of the  $\pi$ -electrons is reduced. Thus reaction between palladium and benzene to give phenylpalladium acetate and subsequent phenylation through this species is the favoured mechanism. Whether all the styrenes used by Yamamura react similarly is, as yet, unknown but  $\beta$ -methylstyrenes with an electron-releasing substituent in the  $\beta$ -position might be expected to form alkenyl complexes and it is possible that an examination of the products could indicate that a mechanism, different to that proposed by Yamamura, is operating.

It is important, therefore, that a more rigorous examination of this system be carried out. Reaction of benzene with equimolar quantities of palladium acetate and  $\beta$ -substituted- $\beta$ -methylstyrenes would afford the monophenylated products which are then available for further phenylation. Reaction of alkene with hexadeuterobenzene



Scheme 40

would show the sites at which phenylation occurs. Reaction of the styrenes used by Yamamura with phenylmercuric acetate and palladium acetate will yield the products formed via phenylpalladium acetate and comparison of the products formed by the various methods might well shed more light on the mechanism of this alkene phenylation.

### 3. STYRENE PHENYLATION ASSISTED BY PALLADIUM (0) OR BY PALLADIUM (II) COMPOUNDS OTHER THAN PALLADIUM (II) ACETATE

#### 3.1 Palladium Metal

When the arylation of styrene with bromobenzene in the presence of palladium acetate was carried out, it was found that, in addition to the expected bromo-trans-stilbenes, trans-stilbene was formed in large amounts (trans-stilbene/bromo-trans-stilbenes; ca. 1:0.4). Formation of trans-stilbene in the above system is similar to a reaction reported by Heck<sup>37</sup> in which olefinic compounds react with aryl, benzyl or styryl halides, in the presence of a catalytic amount of palladium metal (prepared in situ) and a hindered amine, to form vinylic compounds in which a vinylic hydrogen is replaced by the aryl, benzyl or styryl group. Thus the reaction of iodobenzene with styrene and the mechanism proposed by Heck<sup>37</sup> are illustrated in Scheme 40. Oxidative addition occurs between palladium metal and iodobenzene to give the solvated phenyl-palladium iodide (117) which then reacts with styrene, in a manner identical to that described in Scheme 14, to give the adduct (118). Loss of hydridopalladium iodide from (118) affords trans-stilbene and hydrogen iodide which forms an ammonium salt with the amine.

To determine whether the formation of trans-stilbene from bromobenzene and styrene, in the current study, proceeded by reaction of palladium (0), reaction between bromobenzene and palladium



sponge (prepared by reduction of palladium (II) chloride by hydrazine hydrate) was attempted. The formation of trans-stilbene was observed and it is likely, therefore, that reaction proceeds by the mechanism outlined in Scheme 40.

### 3.2 Palladium Propionate

The phenylation of styrene assisted by palladium propionate was performed and the yields of trans-stilbene and triphenylethylene are listed in Table 38.

Table 38    Phenylation of Styrene with Palladium Propionate

Stilbene (%)	TPE (%)	Reaction of Palladium (%)
24.0	45.9	115.8
61.3	4.8	70.9

TPE:- triphenylethylene

Although the results obtained are inconsistent if an attempt were made to optimise the yield of trans-stilbene, then the effect of palladium propionate should be investigated because the yields of each product are as high as those obtained with palladium acetate.

### 3.3 Palladium Benzoate

Styrene phenylation assisted by palladium benzoate was performed. Triphenylethylene was the major product, no trans-stilbene being found. Since very few products volatile by g.l.c. were found, the yield of triphenylethylene was estimated at about 80%, which necessitates that the total reaction of the complex be about 160%. Palladium benzoate, therefore, appears to be a particularly efficient alkene phenylating agent and so this complex should also be used in yield optimisation experiments.

### 3.4 Dichlorobis(benzonitrile)palladium (II)

Attempts were made to phenylate styrene in the presence of dichlorobis(benzonitrile)palladium (II). The yields of trans-stilbene (less than 15%) and triphenylethylene (less than 1%) suggested that styrene phenylation with dichlorobis(benzonitrile)palladium (II) under the present reaction conditions is of little further interest.

### 3.5 Palladium Chloride and Sodium Acetate

Instead of palladium acetate, palladium chloride and sodium acetate were used in styrene phenylation. Styrene was added to a mixture of palladium chloride and sodium acetate in acetic acid which had been heated at 75° for either 0 h or 15 h. The results obtained are in Table 39.

Table 39    Phenylation of Styrene Assisted by Palladium Chloride and Sodium Acetate

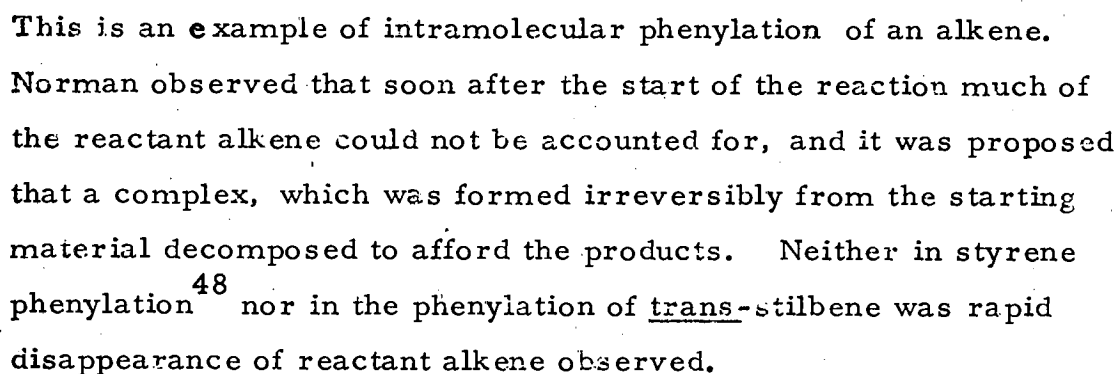
Stilbene (%)	TPE (%)	Reaction of PdCl <sub>2</sub> (%)
9.8	1.4	12.6*
32.9	2.9	38.7
25.1	12.8	50.7
25.8	1.5	28.8




TPE:- triphenylethylene

\* Equilibration time 0 h. For other reactions, equilibration times 15 h.

The yields of trans-stilbene and the total reaction of the palladium compound are not very large and there is the complication that, in the presence of sodium acetate, aromatic acetoxylation becomes important. The use of this system is, therefore, far from ideal for the study of alkene arylation.

The reactions attempted were similar to the cyclisation performed by Norman et al.<sup>44</sup> in which 3, 3, 3-triphenylpropene (119) was cyclised to 1, 1-diphenylindene (120).



(121)                      (122)                      (123)

products, identified by g.l.c. /m.s. and their yields which were measured relative to the smallest product in each reaction mixture are listed in Table 29.

Table 29    Attempted Cyclisation of Alkenes

Alkene	Complex	Product	Yield	Compound
PB (121)	Pd(OAc) <sub>2</sub> <sup>*</sup>	1	34.0	Isomer of PB
		2	2.0	Not identified
		3	1.0	Cyclised product
PB <sup>†</sup> (121)	Pd(OAc) <sub>2</sub>	1	11.0	Isomer of PB
		2	1.2	Isomer of PB
		3	1.3	Cyclised product
		4	1.0	Acetoxyated alkene
PB (121)	Pd(OCOEt) <sub>2</sub>	1	24.0	Isomer of PB
		2	1.3	Not identified
		3	1.5	Cyclised product
		4	1.0	Acetoxyated alkene
AB (122)	Pd(OAc) <sub>2</sub>	1	13.0	Isomer of AB
		2	1.0	Cyclised product
AB (122)	(PhCN) <sub>2</sub> PdCl <sub>2</sub>	1	1.0	Isomer of AB
APE (123)	Pd(OAc) <sub>2</sub>	1	34.0	Not identified
		2	1.0	Not identified
		3	3.6	Cyclised product
APE (123)	(PhCN) <sub>2</sub> PdCl <sub>2</sub>	1	40.0	Not identified
		2	1.0	Isomer of APE
		3	2.4	APE
		4	34.0	Mainly benzonitrile but <u>ca.</u> 5% cyclised product

PB:- 1-phenylbut-2-ene; AB:- allylbenzene; APE:- allylphenyl ether.

\* Palladium acetate batch 2A. Batch 6A in other acetate reactions.

† Reaction time 2.5 h. All other reaction times 3 h.

The cyclised product constitutes a maximum of about only 10% of the products identified. One reason for such low yields is that isomerisation of the alkenes involving movement of the double bond is possible. With 3, 3, 3-triphenylpropene (119), such movement of the double bond cannot occur so cyclisation is favoured to a greater extent.

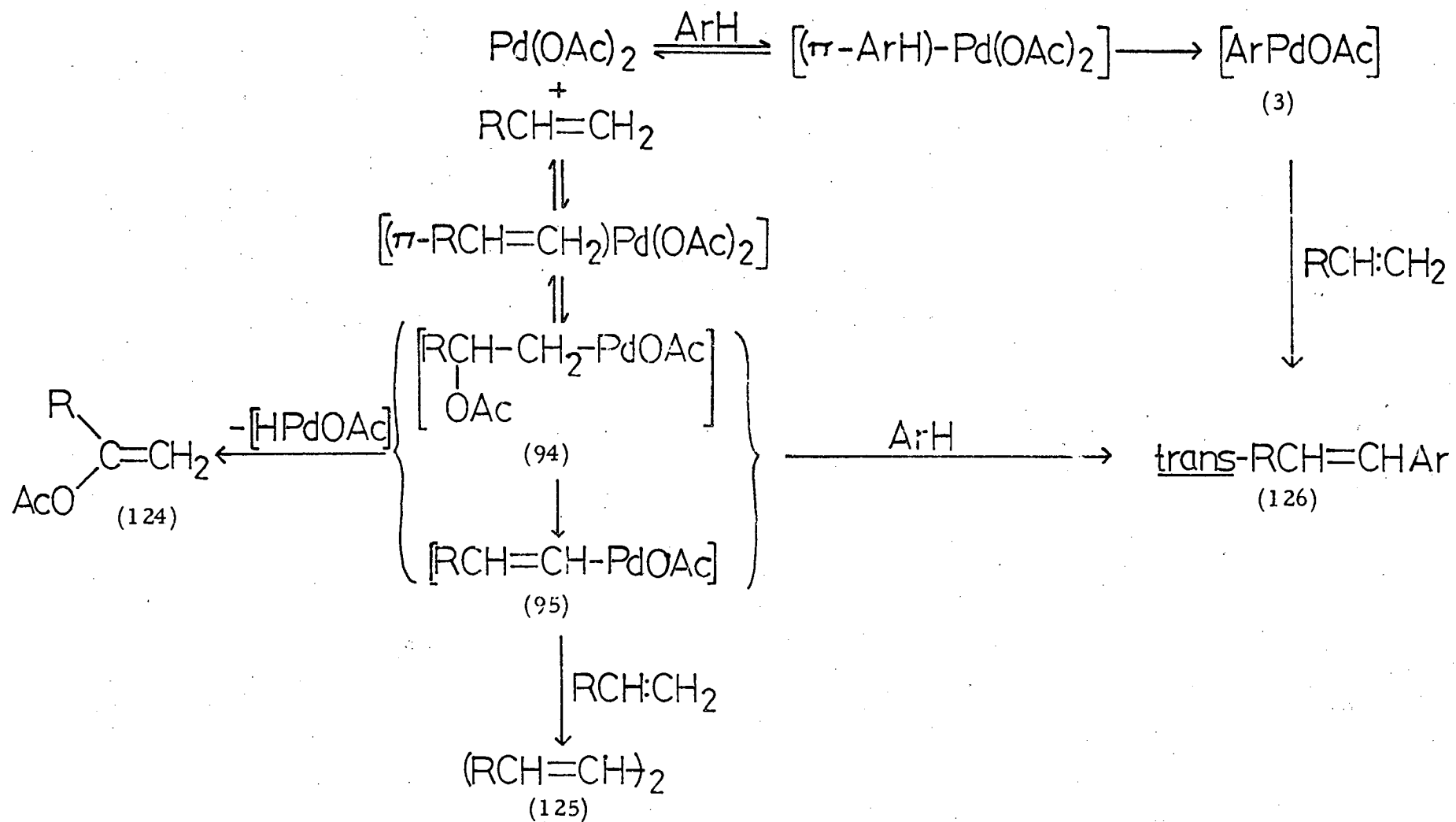
This was only a preliminary study of alkene cyclisation but it demonstrates that although cyclisation can occur it is only likely to be the major pathway with alkenes in which isomerisation is unlikely.

5 CONCLUSION

The original aim of this work was the determination of the mechanism of the palladium (II)-assisted arylation of alkenes. Mechanisms had been suggested by Moritani<sup>18</sup> and by Boyd<sup>48</sup> but it was considered that further investigations were necessary before a mechanism could be proposed with any conviction. In the course of this work it was found that consistent yields of trans-stilbene and triphenylethylene could not be obtained in the phenylation of styrene assisted by palladium acetate and consequently a study of methods of preparation and purification of palladium acetate was undertaken. This resulted in the availability of palladium acetate of a purity capable of producing consistent results over the initial period of alkene arylation. However, a more rigorous study of palladium acetate is necessary to determine the impurities present and to find a method which affords very pure product.

In 1969, Moritani<sup>18</sup> proposed a mechanism for alkene arylation [Scheme 10, p. 76] which involved  $\sigma$ -bond formation between the arene and palladium and between the alkene and the metal, the rate-determining step being that in which  $\sigma$ -bond formation occurred between the alkene and the metal. This mechanism was rejected by Shue<sup>42</sup> because his investigations suggested the slow step to be aryl-to-palladium  $\sigma$ -bond formation, and by Boyd<sup>48</sup> because his results were consistent with Shue's proposal and with the mechanism proposed by Heck for alkene arylation assisted by phenylmercuric acetate and palladium acetate<sup>39</sup> (p. 5).

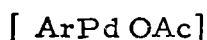
The current study started from the viewpoint that one or more of the four mechanisms described previously (p. 92) could be operating. Much of the work was found to be consistent with all the mechanisms but a few results were explained better by reaction via a  $\sigma$ -acetoxymethyl complex (94), or the corresponding  $\sigma$ -alkenyl species (95), than by any of the other mechanisms, viz. the effect of reactant ratio on the product distribution of styrene



Scheme 41

phenylation and the investigation of the effect of addition of styrene to the phenyl coupling reaction. This led to the proposal that the mechanism operating under the reaction conditions used in the present work is reaction of the aromatic compound with either the alkylpalladium intermediate (94) or the alkenylpalladium species (95). On the basis of the work up to this point it is not possible to distinguish between the two pathways [Scheme 35, p. 111]. If the competitive phenylation of styrene and  $\beta, \beta$ -dideuterostyrene were carried out and the reaction mixture analysed mass spectroscopically for the deuterated and non-deuterated styrenes and stilbenes sufficient information might be gained to distinguish between the two possible reaction routes.

It is accepted that under conditions different from those used in the present study, for example when coordination of alkene to palladium is difficult or when aryl-to-palladium  $\sigma$ -bond formation is facile, alkene arylation via the much-proposed  $\sigma$ -arylpalladium species (3) may occur.



(3)

The overall reaction scheme for arylation, acetoxylation and dimerisation of alkenes under various reaction conditions is illustrated in Scheme 41. Acetoxylation and dimerisation of alkene are visualised as occurring through either or both alkene-derived species (94) and (95) to give the products (124) and (125) respectively. Alkene arylation can occur by either route shown, via the  $\sigma$ -arylpalladium intermediate (3) or via the alkene species (94) and (95) to give the product (126).

Further work still remains to be done to complete the mechanistic investigations. It is suggested that alkene arylation be performed under carbon monoxide in an attempt to trap an intermediate palladium species by insertion of carbon monoxide



into a palladium-carbon  $\sigma$ -bond. It is also proposed that further investigations be carried out into the phenylation of  $\beta$ -substituted- $\beta$ -methylstyrenes, reported by Yamamura et al.,<sup>65</sup> in the hope that the information obtained will shed more light on the applicability of the various mechanisms proposed.

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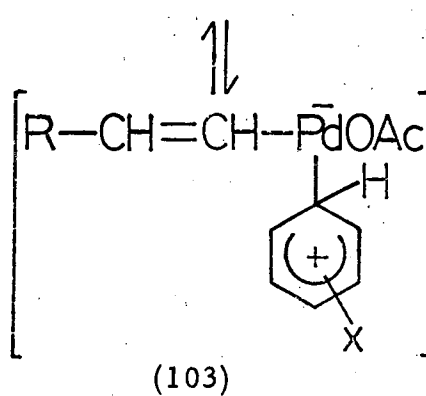
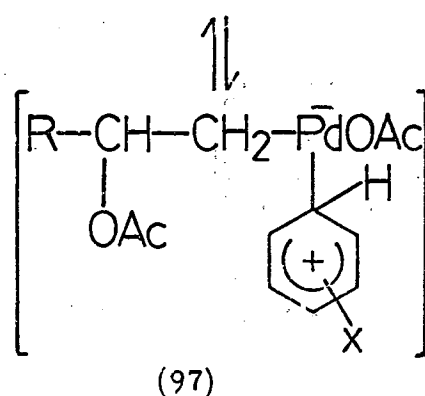
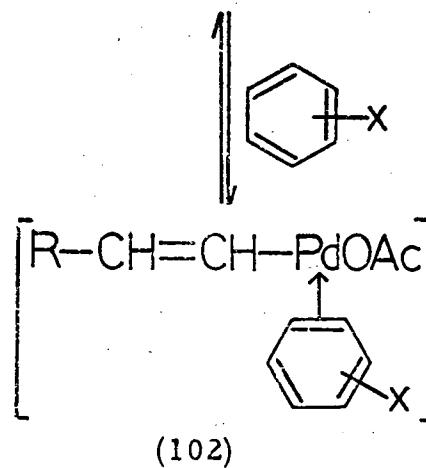
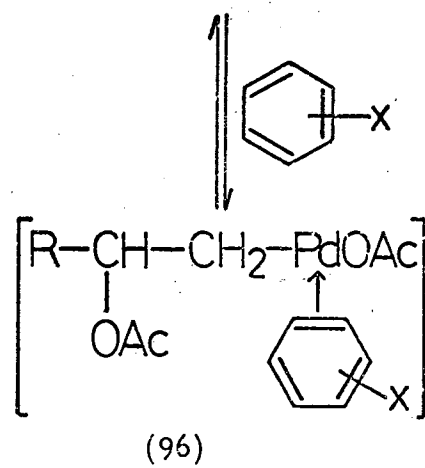
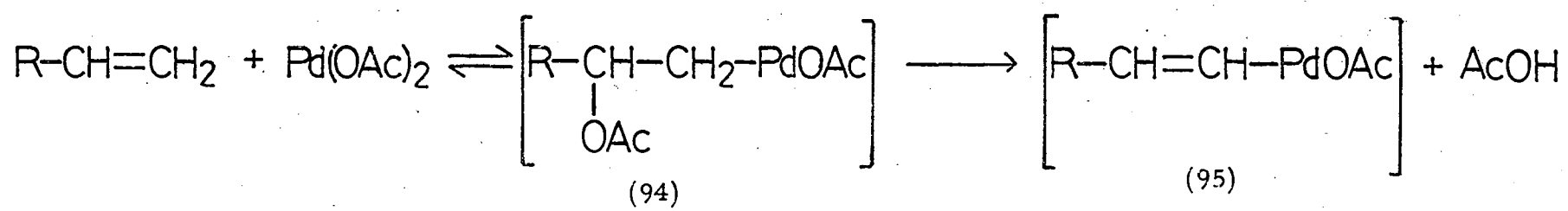
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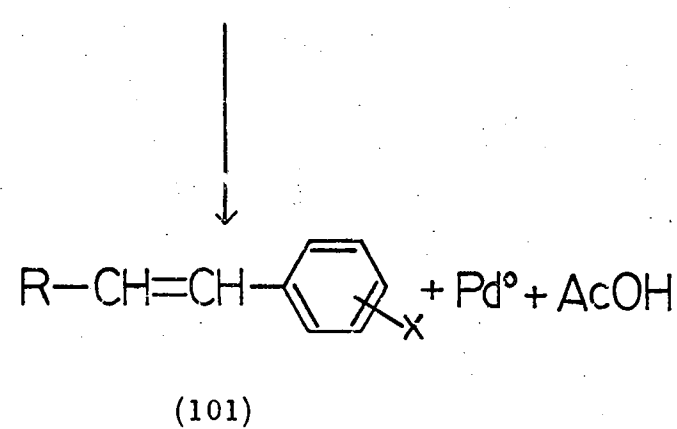
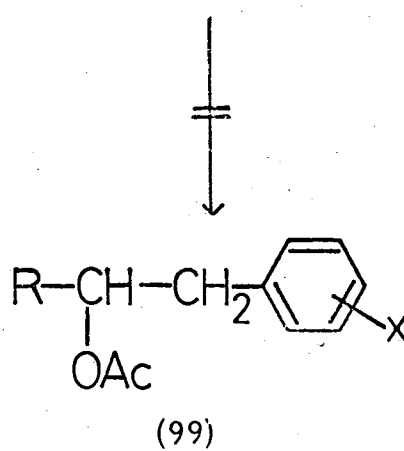
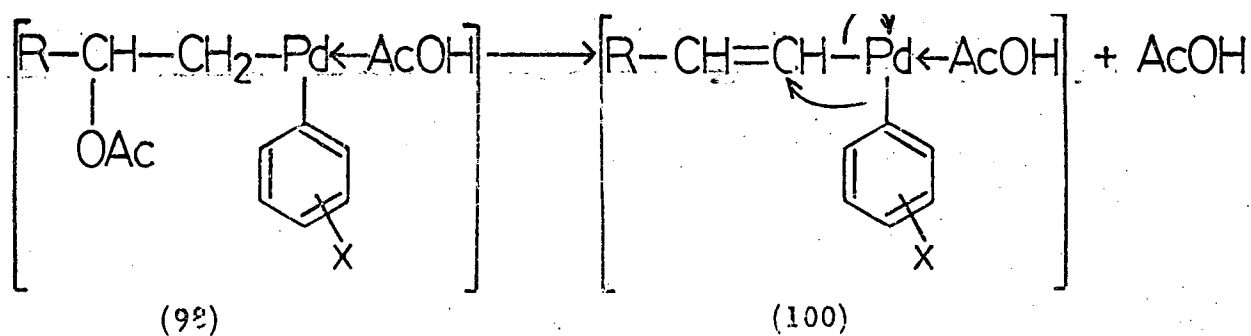
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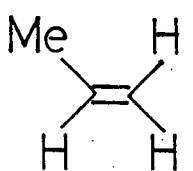
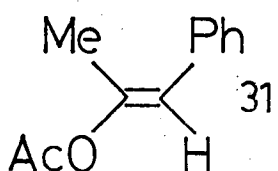
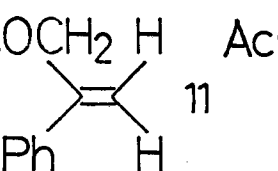
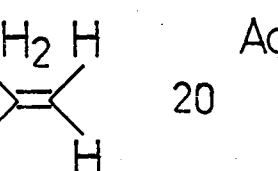
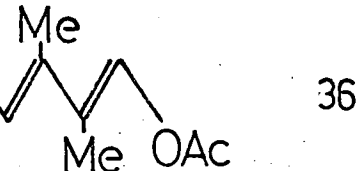
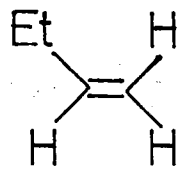
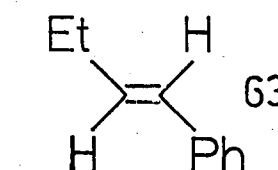
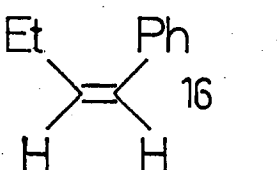
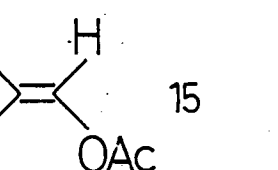
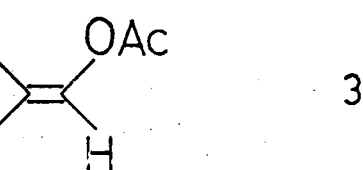
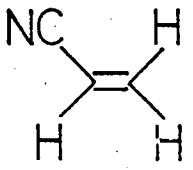
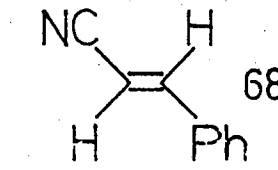
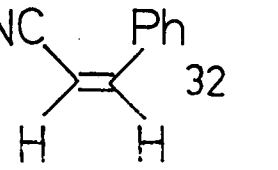
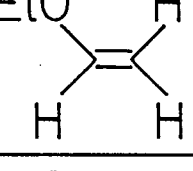
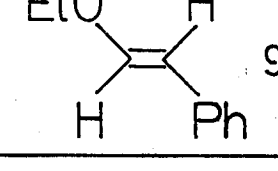
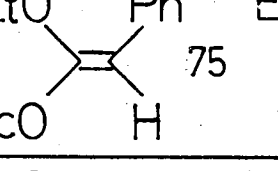
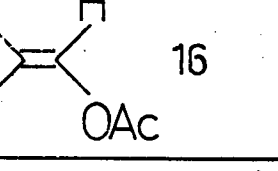
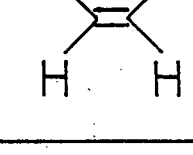
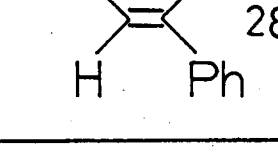
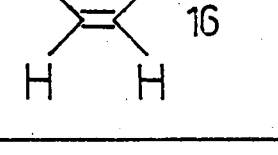
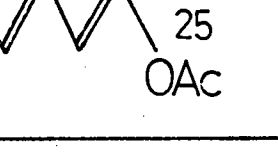
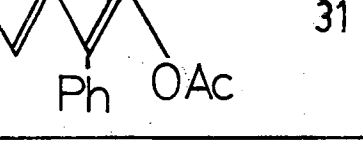
Scheme 35



Table 6

Physical Data of All Batches of Palladium Acetate

	Analysis (%)			Colour Form	Prepara- tion	Purifica- tion	Yield (%)	m. p. (decomp) °C	I. r. Absorptions cm <sup>-1</sup>		
	C	H	N						ω <sub>1</sub>	ω <sub>2</sub>	ω <sub>3</sub>
Required 21.40 2.69 0.00											
Batch	21.4	3.1		O, C	a	none	ca. 100	205	1600	1427	
1	21.52	2.70	0.10	B, C	a 1	IV		202	1610	1440	700
2A	21.38	2.76		B, C	a 1	none	30.0	198	1608	1435	700
2B	18.47	2.31	1.47	B, A	a 2	none	8.5	195	1608	1435	695
3A	20.31	2.55		B, A	a 1	none	61.6	199	1608	1435	697
3B	23.65	2.92		B, A	a 1	I 1		201	1608	1430	698
3C	20.89	2.63	0.42	B, A	a 2	none	4.8	197	1603	1425	695
4A	21.18	2.65		B, C	a 1	none	18.1	201	1603	1440	695
4B	23.85	2.84		B, C	a 1	II 1		199	1603	1435	698
4C	21.60	2.70		B, C	a 2	II 1	13.4	201	1605	1440	700
4D	22.50	2.83		B, A	a 1	III		200	1608	1435	698
4E	21.38	2.68	0.15	P, C	a 1	II 1		203	1603	1438	700
5A	20.78	2.65	0.53	B, C	a 1	none	33.6	197	1605	1430	698
5B	22.29	2.80	0.34	B, C	a 2	II 1	8.6	200	1610	1435	700
6A	21.03	2.67	0.36	B, A	b 1	none	41.5	201	1610	1435	700
6B	20.43	2.57	0.60	B, A	b 2	none	9.2	196	1605	1433	700
7	19.59	2.46	1.06	B, A	b 1	none	51.7	195	1605	1433	695
8	14.62	1.90	1.89	B, A	a *	IV 1	16.7	192	1620	1423	695
9A	20.65	2.62		R, A	a *	IV 1	4.6	190	1620	1425	698
9B	21.16	2.64	0.13	B, C	a *	IV 2	10.4	199	1608	1430	698
10	21.36	2.71	0.18	B, C	c 1	none	58.9	202	1603	1440	700
11	21.46	2.75	0.11	B, C	c 1	none	29.8	203	1603	1435	700
12	21.20	2.63	0.09	B, C	c 1	V 1	30.0	199	1605	1435	698
13	21.11	2.71	0.17	B, C	c 1	V 1	37.9	198	1608	1430	700
14A	20.73	2.60	0.25	B, C	e			198	1605	1438	700
14B	21.03	2.57	0.09	B, C	e	VI 1		200	1603	1440	700

Alkene	Product Distribution %	Total Yield %
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	 63  16  15  3	21
	 68  32	25
	 9  75  16	13
	 28  16  25  31	

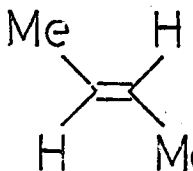
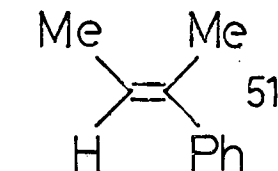
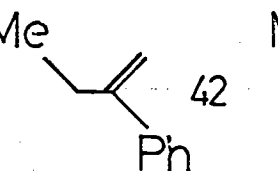
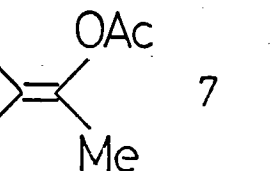
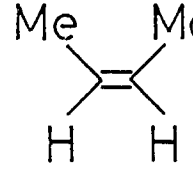
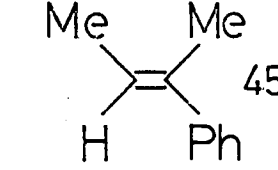
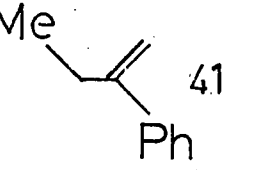
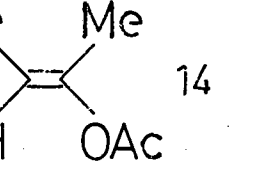
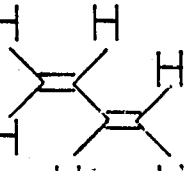
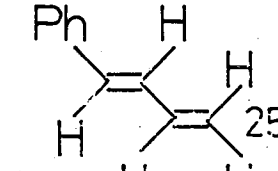
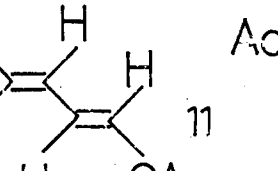
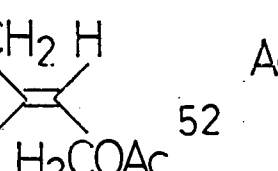
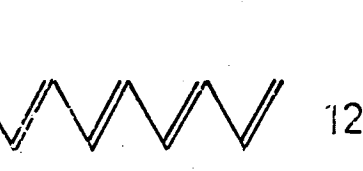
	 51  42  7	26
	 45  41  14	26
	 25  11  52  12	100

Table 5. Reaction of Substituted Alkenes with Benzene<sup>16, 18</sup>